2. DIESEL EMISSIONS, TRANSPORT, AND TRANSFORMATION

2.1. INTRODUCTION

This chapter reviews a number of background topics that are valuable for perspective and context as one considers the health data (in later chapters) for diesel exhaust exposure. The contents of this chapter are not intended to necessarily reflect the most current literature, and thus should not be considered comprehensive and authoritative in that respect.

The diesel engine was patented in 1892 by Rudolf Diesel, who conceived it as a prime mover that would provide much improved fuel efficiency compared with spark-ignition engines. To the present day, the diesel engine's high efficiency remains its strongest selling point. In the United States, the diesel engine is used mainly in trucks, buses, agricultural and other off-highway equipment, locomotives, ships, and many stationary applications.

The chief advantages of the diesel engine over the gasoline engine are its fuel economy and durability. Diesel engines, however, emit more oxides of nitrogen (NO_x) and carbonaceous particulate matter than do gasoline engines. Over the past decade, modifications of diesel engine components have substantially reduced gaseous and particle emissions (Hammerle et al., 1994).

The diesel engine compresses air to high pressure and temperature. Fuel, when injected into this compressed air, autoignites, releasing its chemical energy, and the resulting combustion gases expand, doing work on the piston, before being exhausted to the atmosphere. Power output is controlled by the amount of injected fuel rather than by throttling the air intake. Compared to its spark-ignited (SI) counterpart, the diesel engine's superior efficiency derives from a higher compression ratio and no part-load throttling. Because of its poorer air utilization, a diesel engine requires a larger piston displacement for the same power output as a comparable SI engine. To ensure structural integrity for prolonged reliable operation at the higher peak pressures brought about by a higher compression ratio and autoignition, the structure of a diesel engine generally is more massive than its SI counterpart.

Diesel engines may be broadly identified as being either two- or four-stroke cycle, injected directly or indirectly, and naturally aspirated or supercharged. They also are classified according to service requirements such as light-duty (LD) or heavy-duty (HD) automotive, small or large industrial, and rail or marine engines.

All diesel engines use hydraulic fuel injection in one form or another. The fuel system must meet four main objectives if a diesel engine is to function properly over its entire operating range: (1) meter the correct quantity of fuel, (2) distribute the metered fuel to the correct cylinder, (3) inject the metered fuel at the correct time, and (4) inject the fuel so that it is atomized and mixes well with the in-cylinder air. The first two objectives are functions of a well-designed injection pump, and the last two are mostly functions of the injection nozzle. As a part of the

effort to obtain lower exhaust emissions without diminishing fuel efficiency, fuel injection systems are moving toward the use of electronics for more flexible control than is available with purely mechanical systems.

Both the fuel and the lubricants that are used to service diesel engines are highly finished petroleum-based products combined with chemical additives. Diesel fuel oil is a mixture of many different hydrocarbon molecules from about C_7 to about C_{35}, with a boiling range from roughly $350°F$ to $650°F$. Many of the fuel oil properties, such as its specific energy content, ignition quality, and specific gravity, are related to its hydrocarbon composition. Therefore, fuel and lubricant composition affects many aspects of engine performance, including economy and exhaust emissions. For example, a decrease of fuel aromatic content, sulfur, and volatility usually leads to a reduction of regulated emissions (Ullman, 1989). The four stages of the combustion process in the diesel engine are:

1. Ignition delay period: the elapsed time from the start of injection until the start of combustion. This is the time required to atomize fuel, evaporate droplets, and mix vapor with air and for the necessary preflame reactions to occur. The ignition delay period is really two inseparable overlapping delay periods, physical delay and chemical delay.

2. Uncontrolled burning period: during this stage the fuel that has passed entirely through the first stage autoignites and burns in a premixed fashion and then diffusion takes over control of the burning (Lyn, 1963; Kahn, 1970). During this stage a high rate of pressure rise and noise associated with diesel knock occur.

3. Controlled burning period: during this stage the fuel burns as it is injected in what is essentially a diffusion-controlled process. The burning rate and the rate at which energy is released in this stage are lower than during the second stage.

4. Afterburning period: the elapsed time from the end of fuel injection until the end of combustion. This stage is characterized by the diffusion mode giving way to the premixed mode of combustion.

Diesel emissions are derived from the complete and incomplete combustion of fuel and lubricating oil; they are a mixture of gases and low molecular weight (MW) carbon particles. High MW organic compounds are adsorbed on the particles. Table 2-1 lists the major diesel combustion emissions and their atmospheric reaction products.

Combustion of fuel in the diesel engine results in the formation of a complex mixture of gaseous and particulate exhaust. Because of concerns over possible health effects associated with diesel particulate emissions, measurements have been made to characterize chemically in detail the exhausts from light-duty diesel (LDD) and, to a lesser extent, heavy-duty diesel (HDD)

Table 2-1. Major components of diesel engine emissions and their known atmospheric transformation products

Emission component	Atmospheric reaction products
A. Vapor-phase emissions[a]	
Carbon dioxide	—
Carbon monoxide	—
Oxides of nitrogen	Nitric acid, ozone
Sulfur dioxide	Sulfuric acid
Hydrocarbons Alkanes ($\leq C_{18}$)	Aldehydes, alkyl nitrates, ketones
Alkenes ($\leq C_4$) (e.g., 1,3-butadiene)	Aldehydes, ketones
Aldehydes Formaldehyde	Carbon monoxide, hydroperoxyl radicals
Higher aldehydes (e.g., acrolein)	Peroxyacyl nitrates
Monocyclic aromatic compounds (e.g., benzene, toluene)	Hydroxylated and hydroxylated-nitro derivatives[b]
PAHs (≤ 4 rings)[c] (e.g., phenanthrene, fluoranthene)	Nitro-PAHs (≤ 4 rings)[d]
Nitro-PAHs (2 and 3 rings) (e.g., nitronaphthalenes)	Quinones and hydroxylated-nitro derivatives
B. Particle-phase emissions	
Elemental carbon	—
Inorganic sulfate	—
Hydrocarbons (C_{14}-C_{35})	Little information; possibly aldehydes, ketones, and alkyl nitrates
PAHs (≥ 4 rings) (e.g., pyrene, benzo[a]pyrene)	Nitro-PAHs (≥ 4 rings)[d] Nitro-PAH lactones
Nitro-PAHs (≥ 3 rings) (e.g., nitropyrenes)	Hydroxylated-nitro derivatives

[a]Unless otherwise stated, the impact results from both the emissions components and the atmospheric reaction products.
[b]Some reaction products expected to partition into the particle phase.
[c]PAHs containing four rings are usually present in both the vapor and particle phases.
[d]Nitro-PAHs with more than two rings will partition into the particle phase.

Source: HEI, 1995.

engines. Most of these measurements are of primary pollutants, that is, gases and particulate matter emitted directly into the air from their sources.

The primary pollutants are subject to dispersion and transport and, at the same time, to chemical and physical transformations into secondary pollutants; the time scales of these atmospheric transformations and physical loss processes vary widely. Atmospheric lifetimes range from <1 min for some highly reactive organic compounds to months for other much more inert constituents of direct emissions. Thus, to assess the environmental effects of diesel emissions, it is necessary to determine the chemical and physical changes that primary diesel emissions undergo during their transport through the atmosphere.

Combustion of fuel in the diesel engine results in the formation of a complex mixture of gaseous and particulate exhaust. Because of concerns over possible health effects associated with diesel particulate emissions, measurements have been made to characterize chemically in detail the exhausts from light-duty diesel (LDD) and, to a lesser extent, heavy-duty diesel (HDD) engines. Most of these measurements are of primary pollutants, that is, gases and particulate matter emitted directly into the air from their sources.

The primary pollutants are subject to dispersion and transport and, at the same time, to chemical and physical transformations into secondary pollutants; the time scales of these atmospheric transformations and physical loss processes vary widely. Atmospheric lifetimes range from <1 min for some highly reactive organic compounds to months for other much more inert constituents of direct emissions. Thus, to assess all of the environmental effects of diesel emissions, it is necessary to determine the chemical and physical changes that primary diesel emissions undergo during their transport through the atmosphere.

2.2. OVERVIEW OF DIESEL POLLUTANTS AND POLLUTANT FORMATION
2.2.1. Gas-Phase Pollutant Emissions
2.2.1.1. *Oxides-of-Nitrogen Formation*
Because the diesel combustion process is very complex and involves burning of fuel droplets, it has proven difficult to predict pollutant concentrations or emission rates quantitatively. In SI gasoline engines, NO emission can be quantitatively explained by adiabatic compression of the initially burned mixture (nearest the spark plug) by the combustion pressure developed in the later stages of combustion. Thus, the originally burned gases are raised to a much higher temperature than that achieved in the flame by the subsequent compression. Shahed (1985) has reviewed the work on this subject for diesel engines. He reports that, qualitatively, NO formation in diesel engines cannot be explained by this phenomenon. The time-temperature history of the burning droplets seems to determine the extent of NO formation. Yu and Shahed (1981) have defined relevant engine operating parameters that control NO emissions for heavy-duty diesel

engines. For instance, retarding injection or recirculating exhaust gases reduces NO formation and emission at the expense of increasing soot formation and hydrocarbons, all other factors being equivalent. Wu and Peterson (1986) studied NO formation kinetics in an IDI passenger-car diesel engine over a wide range of operating conditions. These authors found that a variable-temperature model accounting for the average gas temperature at the time of droplet burning explained the observed NO considerably better than a constant-temperature (peak-cycle-temperature) model. Global NO formation rates in their study suggested that the NO must be formed in the vicinity of the droplet flame zone.

Lipkea et al. (1987) and Lipkea and DeJoode (1987) have constructed a successful engine model that adequately explains NO formation. Process parameters that control NO formation include fuel jet momentum flux, in-cylinder air density at the start of injection, swirl cross-flow momentum flux, and in-cylinder temperature. Air system design characteristics that change air density and temperature can result in constant work but decreasing NO_x. On the other hand, decreasing cylinder temperatures also result in increased hydrocarbon emissions (Uyehara, 1987; Gill, 1988). The net result is a tradeoff between NO_x and particulate material at high temperatures and between NO_x and hydrocarbons at low operating temperatures.

2.2.1.2. *Hydrocarbons and Carbon Monoxide Formation*

Small quantities of gaseous unburned hydrocarbons (HCs) and carbon monoxide (CO) are emitted from diesel engines, but less than those emitted by comparable SI engines. Myers and Uyehara (1947) have explained the observed CO on the basis of locally rich combustion. During the ignition delay period, especially small amounts of fuel vaporize from the initial droplets. The gas-phase reactions of this material are responsible ultimately for its ignition and, thus, the ignition of the droplets. However, this premixed patch is likely to be locally quite rich, even though the overall fuel-air mixture has considerable excess air. Therefore, CO is formed in concentrations of 2,000 ppm or even slightly more in diesel exhaust. By comparison, typical gasoline engines might have exhaust CO concentrations of 10,000 to 20,000 ppm.

These locally rich combustion processes are also responsible for a small release of low molecular weight hydrocarbons, principally methane, ethylene, and acetylene, in diesel exhaust. About 10% of these materials are C_1 to C_4 combustion-derived compounds. The bulk of the emission in the gas phase is diesel fuel in the C_{10} to C_{25} molecular weight range; these materials account for 70% to 80% of the HCs emitted. The balance of the material, including particle-bound HC, is in the same molecular weight range as lubricating oil. Similar findings have been reported with HD diesel engines, both of the two-stroke and four-stroke cycle types. Therefore, both fuel and lubricant can supply organic matter to diesel engine exhaust HCs in the gaseous and particulate states.

Hampton et al. (1983) reported a gas chromatography-mass spectrometry (GC-MS) study of heavy HCs in a Pennsylvania Turnpike roadway tunnel that has varying amounts of diesel and gasoline passenger-car traffic. There were characteristic differences in gaseous HC content of the tunnel gases between the diesel and gasoline vehicles. Typically, diesel traffic was characterized by substantial quantities of aliphatic hydrocarbons with lesser amounts of long-chain substituted monoaromatics. Gasoline traffic was dominated by methyl- and ethyl-benzene emissions, based on the porous polymer trapped samples used in this study. These results are in general agreement with the Black and High (1979) conclusion that diesel HC emissions are primarily fuel-derived.

2.2.2. Particle Formation and Emission

The chemical mechanism that accounts for carbon formation in diesel combustion is not completely established; the major weight of scientific opinion seems to support some role for intermediate formation of polycyclic aromatic hydrocarbons in the process. Diffusion flames, whether rich or lean, usually form some carbon. However, carbon is consumed on the lean side by reaction with hydroxyl (OH) radicals (Fenimore and Jones, 1967), and only when the OH radical population is reduced by other reactions (with fuel hydrocarbons, for example) is carbon found to be a major combustion product. Thus, carbon is normally a stable combustion product only of rich flames.

Beck and Uyehara (1988) have pointed out that there is a very good linear correlation between CO emission rate and carbon emission rate from HD engines. Once formed, both substances are difficult to remove, requiring highly energetic OH radicals for reaction. These authors argue that carbon formation normally takes place over a rather narrow temperature range and that the maximum rate of carbon formation is found at temperatures around 2,250 K. At temperatures of 2,400 K and above, carbon is burned out, and at temperatures of 1,900 K and below, it is never formed. However, if attempts are made to raise temperature and thus burn out the carbon, high NO results. If flame zone temperatures are lowered by adding water, alcohol, or exhaust gas, HC emissions are increased (Ball, 1987; Kadota and Henein, 1981). Beck and Uyehara have described a qualitative model of droplet combustion in which the burning rate of fuel droplets is controlled by boiling rate. It is shown that an ideal condition involves high-pressure, high-velocity injection with a minimum ignition-delay period. Carbon can be minimized by reducing rich gaseous combustion and NO can be controlled by delayed-injection timing. Under these conditions, the fuel cetane number might become a critical parameter controlling the ignition delay and the region of uncontrolled combustion. In practice, Ullman (1989) has shown that reducing aromatic content and, hence, decreasing the ignition delay of diesel fuel is beneficial in the control of particulate material and of NO_x emissions in three HD engines built to meet the 1988 California or 1991 Federal emissions standards. Tosaka et al. (1989) have studied the effect

of fuel aromatics in promoting diesel carbon formation. These authors have found an aliphatic radical-benzene condensation process that apparently accounts for the additional amounts of carbon that result in the diesel combustion of aromatic fuels.

2.2.3. Gas-to-Particle Conversion
2.2.3.1. *Condensation of Organic Matter*

Generally, the formation of carbon particles is thought to involve growth of particles by polymerization of gaseous intermediates at the surface of small particles (Kadota and Henien, 1981; Plee et al., 1981). Thus, the growth and agglomeration of carbon particles are probably gas-to-particle processes. Ross et al. (1982) studied the properties of diesel particles obtained from an engine operated on high-purity dodecane. In this case, the fuel was too volatile to have an impact on particle composition. These authors found that the carbon particles contained an HC film, which must have been condensed from the gas phase. The carbon had rather low specific surface area, about 0.5 m^2/g, which could be materially increased by high-temperature treatment.

Heats of sorption of a variety of HCs were determined by a GC technique. It was found that the absorptivity of gaseous organic compounds on these particles was controlled by Henry's law of absorption in the organic surface film. The presorbed organic layer was several layers thick, and this material essentially acted as an organic droplet, dissolving materials from the gas phase. Thus, the heat of sorption was adequately explained by the heat of vaporization of the organics (Ross et al., 1982).

2.2.3.2. *Oxidation of Sulfur Oxides*

Studies of diesel particle composition have produced some information about the fate of fuel sulfur. In the earliest studies, sulfate was found to be a significant component of diesel particles (Hare et al., 1976). Generally, the sulfate found in particles accounted for only about 2% of the fuel sulfur charged, the balance being emitted as sulfur dioxide (SO_2).

Sulfate emission rates have been measured using both engine and chassis dynamometer test procedures. Hare et al. (1976) measured composite particle emission rates on the older Federal compliance test for HD engines and found that with overall emission rates from 0.3 to 1.0 g/kW h (0.4 to 1.3 g/bhp h) of particle mass, sulfate emissions were relatively constant at about 0.02 g/kW h (0.03 g/bhp h). Dietzmann et al. (1980) measured sulfate emission rates from a number of HD vehicles driven over simulated urban driving schedules and found emission rates from about 0.03 to 0.05 g/km for overall particle emission rates from 0.5 to 1.6 g/km. Thus, with previous engines, sulfate was a significant but small (2% to 3%) component of diesel particle mass. With newer engine designs and particle emission rates characteristically below 0.25 g/bhp

h, this emission rate amounts to 10% to 15% of the emitted particle mass, a very important portion of the allowable limit. Currently, no means of reducing this sulfate formation is available other than reducing the sulfur concentration of diesel fuel.

Earlier in this document, the evidence regarding the oxidation of nitrogen to nitric oxide was documented. Dietzmann et al. (1980) have reported analysis of HD diesel vehicle exhaust for NO_2 during simulated urban driving. These authors have reported NO_2 concentrations from about 1 to 5 ppm, accounting for 2% to 5% of the NO emitted. Harris et al. (1987) have measured NO_2 and HNO_3 in air-diluted diesel exhaust. In the exhaust from HD engines, the NO_2 concentration was from 1 to 30 ppm, whereas the HNO_3 ranged from 0.08 to 0.8 ppm. Generally, HNO_3 accounted for a few percentage points of the NO_2, which in turn accounted for a few percentage points of the NO.

2.2.4. Nitroarene Formation

The soluble extract from diesel-generated particulate material was shown to cause mutations when subjected to a bacterial assay (Huisingh et al., 1978). It was not long before evidence began to point toward the class of compounds consisting of nitrated polycyclic aromatic hydrocarbons (PAHs) that have come to be called nitroarenes (Pederson and Siak, 1981; Newton et al., 1982). Hare and Bradow (1979) reported a summary of the EPA findings to that date on the formation of semipolar mutagens in both HD and LD diesel engines. Dietzmann et al. (1980, 1981) reported emissions of mutagenic material from a variety of HD trucks operated over transient driving cycles, and Gibbs et al. (1980) reported the emission of bacterial mutagens from a large number of in-use diesel passenger cars.

Very-high-resolution organic analytical procedures have been applied to diesel exhaust samples (Liberti et al., 1984; Schuetzle and Frazier, 1986; Schuetzle and Perez, 1983). Generally, a variety of nitrated polycyclic aromatic compounds has been found, which accounts for a substantial portion of the mutagenicity found. However, not all the bacterial mutagenicity has been identified in this way, and the identity of the remainder of the mutagenic compounds remains unknown. The nitrated aromatics thus far identified in diesel exhaust were the subject of review in the International Agency for Research on Cancer (1989) monograph on diesel exhaust (Table 2-2).

2.3. PRIMARY DIESEL EMISSIONS

Detailed chemical characterization of diesel engine emissions was performed mostly in the late 1970s and early 1980s. Since that time substantial changes have occurred in engine and emission control technologies, as well as in chemical analysis methodology. It is likely that emissions from currently manufactured diesel vehicles are not the same as those measured and

Table 2-2. Some nitroarenes identified in vehicle exhaust[a]

1,3-Dihydroxynitropyrene-1
2,5-Dinitrofluorene
2,7-Dinitrofluorene
2,7-Dinitro-9-fluorenone
1,3-Dinitropyrene
1,6-Dinitropyrene
1,8-Dinitropyrene
9-Methylcarbazole
1-Nitro-3-acetoxypyrene
9-Nitroanthracene
2-Nitroanthracene or -phenanthrene
x-Nitroanthracene or -phenanthrene (two isomers)[b]
6-Nitrobenzo[a]pyrene
x-Nitrobenzoquinoline[b]
2-Nitrobiphenyl
3-Nitrobiphenyl
4-Nitrobiphenyl
1-Nitrochrysene
x-Nitrodibenzothiophene (two isomers)[b]
x-Nitro-y,z-dimethylanthracene or -phenanthrene (five isomers)[b]
1-Nitrofluoranthene
3-Nitrofluoranthene
7-Nitrofluoranthene
8-Nitrofluoranthene
2-Nitrofluorene
3-Nitro-9-fluorenone
10-Nitro-1-methylanthracene or -phenanthrene
10-Nitro-9-methylanthracene or -phenanthrene
x-Nitro-y-methylanthracene or -phenanthrene[b]
1-Nitro-2-methylnaphthalene
3-Nitro-1-methylpyrene
6-Nitro-1-methylpyrene
8-Nitro-1-methylpyrene
1-Nitronaphthalene
2-Nitronaphthalene
2-Nitrophenanthrene
1-Nitropyrene
5-Nitroquinoline
8-Nitroquinoline
x-Nitroterphenyl[b]
x-Nitro-y,z,z′-trimethylanthracene or -phenanthrene (six isomers)[b]
x-Nitrotrimethylnaphthalene (three isomers)[b]

[a]From International Agency for Research on Cancer, 1989.
[b]x, y, z, and z′ imply position is unknown.

reported earlier. When possible, the latest data were used; however, the data presented in this chapter should not be considered fully representative of emissions from the wide range of diesel engines currently used or those that may have occurred in the past.

2.3.1. Gaseous Emissions

Diesel passenger-car and light-truck emissions of CO and total gaseous hydrocarbons (THC) are considerably lower than those of gasoline vehicles. For HDD vehicles, the CO and THC emission rates are somewhat lower than, but comparable with, those of HD gasoline vehicles, but NO_x emissions are many times those of average traffic. In addition to these regulated pollutants, diesel exhausts also contain some sulfur dioxide because of the presence of sulfur in the diesel fuel. Following combustion, approximately 98% of the sulfur is emitted as SO_2 and 2% as particulate sulfate (Pierson et al., 1978, 1979; Truex et al., 1980). Most of the sulfate is in the form of sulfuric acid (H_2SO_4) (Truex et al., 1980).

The atmospheric concentration of nitric acid (HNO_3) from LDD exhausts has been reported to be negligible in comparison with that from other anthropogenic sources (Okamoto et al., 1983; Harris et al., 1987). A range of concentrations from ≈ 100 ppbv (≈ 250 µg/m^3) to ≈ 800 ppbv (≈ 2 mg/m^3) (Harris et al., 1987) and an emission rate of ≈ 1.3 mg/km were reported (Okamoto et al., 1983).

A small amount of ammonia was also detected in diesel engine exhausts (Pierson and Brachaczek, 1983a). The highest value for NH_3 (25 mg/km) was reported for HDDs; ≈ 4 mg/km was reported for LDD, and ≈ 10 mg/km and ≈ 5 mg/km for gasoline-powered vehicles, with and without catalyst, respectively (Pierson and Brachaczek, 1983a). The emission rates of total aliphatic amines were reported to be below the detection limit of 0.04 to 0.3 mg/km for gasoline-powered vehicles and 0.08 to 0.7 mg/km for heavy-duty trucks. It was concluded that motor vehicles are an insignificant source of atmospheric NH_3 and that amines emitted from motor vehicles cannot give rise to carcinogenic nitrosoamines in the amount said to exist in ambient samples (Pierson and Brachaczek, 1983a).

In addition, low concentrations of phenols have been reported in HDD and LDD emissions (Hare and Baines, 1979; Hare and Bradow, 1979). Aliphatic carboxylic acids (mainly formic, acetic, propionic, and benzoic acids) were also reported in vehicle exhausts (Kawamura et al., 1985; Rogge et al., 1993).

Table 2-3 compares the emission rates of some representative alkanes, alkenes, aromatic hydrocarbons, and aldehydes from HDD and LDD engines and gasoline engines with and without a catalytic converter. Data on catalyst-equipped gasoline vehicles were obtained with a chassis dynamometer and are averaged from 46 in-use passenger cars, 1975 to 1982 models, selected to be representative of vehicles actually driven by the U.S. public (Sigsby et al., 1987). Table 2-3

Table 2-3. Emission rates of volatile organic compounds (VOC) from diesel and gasoline engines

VOC	VOC (g/mi [g/km])			
	Diesel		Gasoline	
	HDD	LDD[a]	Catalyst[b]	Noncatalyst[c]
THC	3.65 (2.28)[d]	0.23 (0.14)[e]	1.8 (1.2)	5.4 (3.4)
Methane	NA	0.01 (0.008)	0.26 (0.16)	0.27 (0.17)
Ethylene	NA	0.04 (0.03)	0.14 (0.09)	0.3 (0.2)
Acetylene	NA	NA	0.04 (0.02)	0.26 (0.16)
Propylene	NA	0.01 (0.008)	0.04 (0.03)	0.15 (0.09)
n-Pentane	NA	NA	0.03 (0.02)	0.09 (0.06)
iso-Pentane	NA	NA	0.07 (0.04)	0.27 (0.17)
n-Decane	0.01 (0.007)[f]	NA	0.003 (0.0016)[g]	
n-Dodecane	0.027 (0.017)[f]	NA	0.003 (0.002)[h]	
Benzene	0.024 (0.015)[d]	0.02 (0.015)[I]	0.06 (0.04)	0.31 (0.19)
Toluene	0.01 (0.007)[f]	0.006 (0.004)[e]	0.1 (0.07)	0.7 (0.45)
Xylenes	0.006 (0.004)[d]	0.002 (0.001)[e]	0.08 (0.05)	0.96 (0.6)
Ethyl benzene	0.005 (0.003)[f]	0.001 (0.0006)[e]	0.02 (0.01)	0.21 (0.13)
Naphthalene	0.01 (0.007)[f]	0.003 (0.002)[e]	NA	NA
Formaldehyde	NA	0.02 (0.01)	0.025 (0.015)	0.06 (0.04)[I]
Acetaldehyde	NA	0.007 (0.004)[e]	0.01 (0.007)	NA
Acrolein	0.053 (0.033)[d]	0.01 (0.006)	0.002 (0.001)	NA
Benzaldehyde	NA	NA	0.003 (0.002)	NA
Total aldehyde	NA	0.03(0.02)[e]	0.04 (0.03)	NA

HDD = Heavy-duty diesel.
LDD = Light-duty diesel.
NA = Data not available.

[a] From National Research Council (1982), except as indicated.
[b] From Sigsby et al. (1987).
[c] From Bailey et al. (1990), except as indicated.
[d] From Westerholm et al. (1991).
[e] From Smith (1989) and Smith and Paskind (1989); four-cycle FTP test, 1986 Mercedes Benz.
[f] From Hampton et al. (1983), data from Allegheny Mountain Tunnel.
[g] From Hampton et al. (1983), no differentiation between vehicles with and without catalyst.
[h] From Hampton et al. (1983).
[I] From Schuetzle and Frazier (1986).

shows the data from the Federal Test Procedure (FTP) only (which attempts to simulate a typical urban driving pattern with average speed of ≈20 mph), although two other driving cycles (Crowded Urban Expressway and the New York City cycle) are reported in the original publication.

The emission data on noncatalyst gasoline vehicles shown in Table 2-3 are averaged from 25 in-use passenger cars, representing late 1980s vehicles in intensive use in the United Kingdom (U.K.) (Bailey et al., 1990). The vehicles were driven "as received" and fueled by leaded premium-grade gasoline, obtained locally from a single source. They were driven on five routes chosen to cover the normal range of U.K. driving speeds and conditions, and the exhaust samples were taken using a miniaturized constant-volume exhaust gas sampler. To allow direct comparison, the urban roadway data (≈13.5 mph average speed) are given in Table 2-3. However, it has to be pointed out that hydrocarbon emission rates are highly dependent on driving speeds; in general, THC emission rate expressed in grams per traveled distance decreases as the driving speed increases, but the individual hydrocarbons display various patterns, which relate to their origin. The gasoline components (hydrocarbons with carbon number $C \geq 4$) are present in highest proportion at low speeds, whereas at higher speeds these components are more efficiently used and the proportion of combustion-derived products increases.

The data on LDD emissions are from the National Research Council report (1982) and from studies (Smith, 1989; Smith and Paskind, 1989) concerning the evaluation of particle trap efficiencies for two diesel passenger cars (a 1986 Mercedes Benz and a Volkswagen prototype Jetta). However, little has been published recently; most of the available data are from the late 1970s and early 1980s.

Quantitative data on emissions from heavy-duty vehicles are relatively sparse and are generally expressed in terms of grams per unit work performed by HDD engines. Most of the data on HDD vehicle emission rates expressed in terms of grams per traveled distance were obtained from tunnel field experiments, in particular from the Allegheny and Tuscarora Mountain Tunnel experiments (Hampton et al., 1982, 1983). Unfortunately, because of the sampling method selected, no quantitative data on hydrocarbons with carbon number $C < 8$ could be obtained.

Recently, exhaust emissions from a HDD truck (Scania 143H, equipped with a turbo-charged Scania DSC 1403 diesel engine) were characterized chemically and tested for mutagenicity during transient driving conditions on a chassis dynamometer (Westerholm et al., 1991). Table 2-3 gives selected data from this study.

As can be seen from Table 2-3, the emissions of gaseous organic compounds from diesel engines and spark-ignition engines are qualitatively similar (e.g., similar chemical components are present in both exhausts), although there are significant quantitative differences. In theory,

new spark-ignition vehicles equipped with catalytic converters emit almost no reactive hydrocarbons in their exhausts. However, catalyst deterioration over the lifetime of the vehicle and evaporative and refueling emissions will result in an increase in the amount of reactive material released.

Table 2-3 lists the emission rates for exhaust pipe emissions only. Currently, fuel evaporation (e.g., from fuel lines and carburetors) accounts for 30% to 60% of the total hydrocarbon emissions from passenger gasoline vehicles with and without catalytic converters (International Agency for Research on Cancer, 1989). Under ambient conditions, the vapor pressure of most diesel fuels in current use is so low that emissions resulting from evaporation are not significant. However, for both diesel and gasoline engine emissions, methane, ethane, ethylene, acetylene, propane, and propylene originate strictly from tailpipe emissions, as evidenced by the fact that the lowest molecular weight components of gasoline are normally hydrocarbons with carbon number C_4.

Differences in the quantity of emitted material between vehicles of the same category are very significant, and such differences arise from many factors of engine design, fuel control, engine conditions, and the general condition of the vehicle at the time of test. The differences between test parameters (e.g., speed, cold or hot start, fuel composition, dynamometer or road measurements, etc.) make the comparison of the data given in Table 2-3 more uncertain. However, it is clear from these data that the emission profile of gaseous organic compounds is different for diesel and spark-ignition vehicles; the aromatic hydrocarbons and low molecular weight alkanes ($<C_9$) are more characteristic of spark-ignition vehicle emissions, whereas the heavier alkanes ($>C_{10}$) are more characteristic of diesel emissions (Hampton et al., 1983; Carey and Cohen, 1980).

2.3.2. Particulate Emissions
2.3.2.1. *Diesel Particulate Matter*
Diesel exhaust particles are aggregates of spherical primary particles, and 75% to 95% of the particulate mass is in the accumulation mode centered about an aerodynamic diameter of 0.2 µm. Figure 2-1 shows a typical size distribution of diesel exhaust particles. The size distribution is important, because transport of the particles in the atmosphere and deposition in the human respiratory tract depend essentially on aerodynamic diameter (see Chapter 4 for discussion of deposition).

Diesel particulate matter is generally defined as any material that is collected on a filtering medium at a temperature of 52°C or less after dilution of the raw exhaust. In general, diesel engines produce more particulate emissions than do gasoline engines with or without catalytic converters. The main constituent of diesel particles is carbon, which accounts for ≈80%
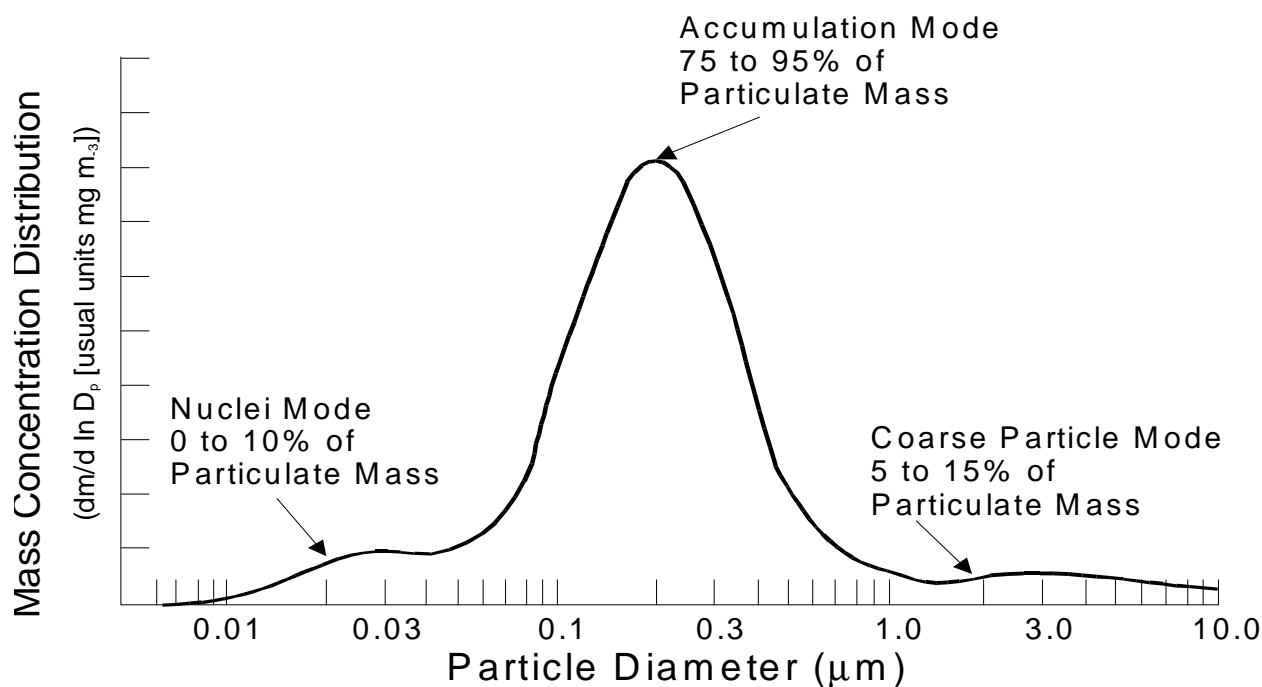
Figure 2-1. Typical size distribution of diesel exhaust particles.

Source: National Research Council (1982).

of total particle mass. Approximately 70% of this so-called total carbon (TC) occurs in the form of elemental carbon (EC); the rest is in the form of organic compounds and is called organic carbon (OC). Table 2-4 compares the emission rates of particulate matter and its distribution between TC and OC for HDD, LDD, and gasoline engines. Data on HDD, LDD, and gasoline engines without catalytic converters are mostly from the survey of 13 HDD vehicles, 19 LDD vehicles, and 22 spark-ignition vehicles in intensive use in Sydney, Australia (Williams et al., 1989a,b). The vehicles were tested on a dynamometer using several test procedures, but Table 2-4 lists the data from the ADR 37 cycle (for spark-ignition and LDD vehicles) and from the modified ADR 36 cycle (for HDD vehicles; multimode steady-state procedure). In addition, data from a heavy-duty truck (Scania 143H), tested on a chassis dynamometer using transient driving conditions (Westerholm et al., 1991), are also given in Table 2-4.

Because the dynamometer studies are not fully representative of the road conditions, the data obtained from the field experiments in two highway tunnels, the Allegheny and Tuscarora Mountain Tunnels of the Pennsylvania Turnpike (Pierson and Brachaczek, 1983b; Szkarlat and Japar, 1983), are also given in Table 2-4 for comparison. Table 2-5 lists the particle-phase and

Table 2-4. Particulate matter emission rates and their distribution between total carbon (TC) and organic carbon (OC) for heavy-duty diesel (HDD), light-duty diesel (LDD), and gasoline engines

Emission	HDD	LDD	Noncatalyst	Catalyst
Particulate matter in g/mi (g/km)	3.2 (2)[a] 1.4 (0.87)[d] 0.99 (0.62)[e]	0.6 (0.37)[a]	0.1 (0.07)[b]	0.02 (0.01)[c]
			0.04 (0.025)[d]	
TC (% w/w)	78[a]	80[a]	31[b]	NA
			67[f]	
OC (% of TC)	58[a] 30[d]	36[a]	87[b]	NA

[a]From Williams et al. (1989b).
[b]From Williams et al. (1989a).
[c]From Schuetzle and Frazier (1986).
[d]From Pierson and Brachaczek (1983b).
[e]From Westerholm et al. (1991).
[f]From Szkarlat and Japar (1983).
NA = Not available.

gaseous-phase emissions of diesel exhaust, along with their atmospheric reaction products (discussed in Section 2.4).

2.3.2.2. *Particulate-Phase Inorganics*

Organic and elemental carbon account for ≈80% of the total particulate matter mass. The remaining 20% is composed of sulfate (mainly H_2SO_4) (Pierson and Brachaczek, 1983b) and some inorganic additives and adventitious components of fuel and motor oil. Table 2-6 gives the average compositions of inorganic constituents of airborne particulate matter associated with vehicles on the road (from Pierson and Brachaczek, 1983b). All airborne constituents of particulate matter associated with vehicle traffic (other than atmospheric transformation products of primary emissions) are included, whether emitted from the exhaust or not (e.g., originated from tire wear debris and soil dust).

2.3.2.3. *Particulate-Phase Organic Compounds*

Carbonaceous, diesel-emitted particles have high specific surface areas of 30 to 50 m^2/g (Frey and Corn, 1967). Because of this high surface area, diesel particles are capable of adsorbing relatively large quantities of organic material originating from unburned fuel and lubricating oil and from pyrosynthesis occurring during combustion of fuel (see Section 2.1).

Table 2-5. Particle phase and gaseous phase emissions from diesel exhaust, and their atmospheric reaction products

Emission component	Atmospheric reaction products
Particle-phase emissions	
Elemental carbon	—
Inorganic sulfate	—
Hydrocarbons (C_{14}-C_{35})	Little information; possibly aldehydes, ketones, and alkyl nitrates
PAHs ($\geq$4 rings) (e.g., pyrene, benzo[*a*]pyrene)	Nitro-PAHs ($\geq$4 rings); nitro-PAH lactones
Nitro-PAHs ($\geq$3 rings) (e.g., nitropyrenes)	Hydroxylated-nitro derivatives
Gaseous-phase emissions	
Carbon dioxide	—
Carbon monoxide	—
Oxides of nitrogen	Nitric acid, ozone
Sulfur dioxide	Sulfuric acid
Hydrocarbons	
Alkanes ($\leq C_{18}$)	Aldehydes, alkyl nitrates, ketones
Alkenes ($\leq C_4$) (e.g., 1,3-butadiene)	Aldehydes, ketones
Aldehydes	
Formaldehyde	Carbon monoxide, hydroperoxyl radicals
Higher aldehydes (e.g., acrolein)	Peroxyacyl nitrates
Monocyclic aromatic compounds (e.g., benzene, toluene)	Hydroxylated and hydroxylated-nitro derivatives
PAHs ($\leq$4 rings) (e.g., phenanthrene, fluoranthene)	Nitro-PAHs ($\leq$4 rings)
Nitro-PAHs (2 and 3 rings) (e.g., nitronaphthalenes)	Quinones and hydroxylated-nitro derivatives

Source: Health Effects Institute (1995).

After removal of extractable organic material, the surface area of diesel particles increases up to 90 m^2/g (Pierson and Brachaczek, 1976).

The extractable fraction of diesel particles is typically in the range of 20% to 30%, but it may be as high as 90% (Williams et al., 1989b) depending on vehicle type and operating conditions. In general, if a diesel engine is running under low load, the incomplete combustion results in a relatively low particle concentration and a higher proportion of organic-associated particles (Dutcher et al., 1984). In addition, recent progress in in-cylinder particulate matter

Table 2-6. Summary of composition and emission rates (in milligrams per kilometer) of airborne particulate matter from on-road vehicles, Tuscarora Mountain Tunnel 1977 experiment

Constituent	Gasoline[a] (mg/km [% of total mass])	Diesel[b] (mg/km [% of total mass])
H	5 ± 4 (10 ± 6)	47 ± 11 (5 ± 1)
B	0.04 ± 0.6 (0.07 ± 0.11)	1.14 ± 0.16 (0.13 ± 0.02)
C	34 ± 21 (67 ± 42)	725 ± 117 (84 ± 14)
N	1.1 ± 0.8 (2 ± 2)	16 ± 2 (1.9 ± 0.3)
Na[c]	0.09 ± 0.37 (0.2 ± 0.7)	6.6 ± 1.0 (0.8 ± 0.1)
Mg[c]	0.7 ± 0.3 (1.3 ± 0.6)	8 ± 1 (0.9 ± 0.15)
Al[c]	0.2 ± 0.5 (0.3 ± 0.9)	8.5 ± 1 (1.0 ± 0.2)
Si[d]	0.5 ± 0.7 (1.0 ± 1.3)	14 ± 2 (1.6 ± 0.2)
P[e]	0.07 ± 0.06 (0.13 ± 0.11)	1.3 ± 0.2 (0.15 ± 0.02)
$S[SO_4^{-2}]$	$0.4[3.4 \pm 0.9]$ $(0.9[7 \pm 3])$	$23[42 \pm 5]$ $(2.7[4.9 \pm 0.9])$
Cl[f]	0.8 ± 0.4 (1.6 ± 0.8)	0 (0)
K[d]	0.17 ± 0.08 (0.3 ± 0.2)	1.5 ± 0.2 (0.17 ± 0.03)
Ca[c]	1.3 ± 0.3 (2.5 ± 0.7)	5.8 ± 1.4 (0.7 ± 0.2)
Ti[d]	0.006 ± 0.01 (0.01 ± 0.02)	0.12 ± 0.03 (0.014 ± 0.004)
Mn[c,f]	0.08 ± 0.01 (0.16 ± 0.025)	0.34 ± 0.04 (0.04 ± 0.004)
Fe[c]	0.32 ± 0.32 (0.6 ± 0.6)	5.0 ± 0.9 (0.6 ± 0.1)
Cu	0.04 ± 0.02 (0.07 ± 0.03)	0.22 ± 0.09 (0.025 ± 0.01)
Zn[e]	0.04 ± 0.04 (0.08 ± 0.08)	1.4 ± 0.1 (0.16 ± 0.1)
Br[f]	5.75 ± 0.45 (11.2 ± 0.9)	0 (0)
Ba[f]	0.03 ± 0.01 (0.07 ± 0.02)	0.66 ± 0.03 (0.08 ± 0.033)
Pb[f]	12.4 ± 1.6 (24)	11.5 ± 3 (1.3 ± 0.3)

[a]Mostly passenger cars, no distinction between catalytic and noncatalytic vehicles.
[b]Mostly heavy-duty diesel trucks, average weight≈30 ton.
[c]Partially attributable to soil dust.
[d]Wholly attributable to soil dust.
[e]Attributable to motor oil.
[f]Attributable to fuel additives.

Source: Pierson and Brachaczek, 1983b.

control has been most effective in reducing the elemental carbon fraction of the particulate matter, so that the organic carbon fraction now accounts for a much larger share than it had previously.

The extractable portion of total carbon, although commonly used as a measure of organic compound content, is not totally equivalent to the OC fraction, as measured by the thermal-optical carbon analysis technique (Japar et al., 1984). The average ratio of OC to extractable mass was shown to be 0.70 ± 0.05, when toluene/propanol-1 mixture was used as an extraction solvent, and this ratio was probably the result of the presence of both oxygenated organic compounds and inorganic sulfates in the extracted mass.

2.3.2.3.1. *Extraction and fractionation techniques.* A variety of solvents and extraction techniques have been used in the past for the separation of organic compounds from diesel particles (Levsen, 1988). Although the reports on the extraction efficiencies are in part contradictory, it appears that Soxhlet extraction and the binary solvent system composed of aromatic solvent and alcohol gave the best recovery of PAHs, as determined by ^{14}C-B[*a*]P (benzo[*a*]pyrene) spiking experiments (Schuetzle and Perez, 1981). Direct chemical analysis of the entire extractable fraction of diesel particulate matter is not generally possible because a large number of compounds of different polarity are present. The separation of diesel particulate organic matter (POM) into various fractions according to chemical functionalities is a necessary preliminary step to chemical identification of individual compounds. Open-column liquid chromatography (LC) and liquid-liquid separation procedures have been the most widely used fractionation methods (Lee and Schuetzle, 1983). Open-column LC is very often followed by normal-phase high-performance liquid chromatography (HPLC) if the identification of less abundant components is required.

2.3.2.3.2. *Chemical composition*. Table 2-7 lists the general classes of extractable organic compounds identified in POM from combustion emissions, including diesel emissions.

Liquid chromatography methods usually divide the complex environmental mixtures of organic compounds into nonpolar, moderately polar, and polar fractions. This separation is

Table 2-7. Classes of organic compounds identified in particulate-phase combustion emissions

Hydrocarbons
Derivatives[a] of hydrocarbons
Polycyclic aromatic hydrocarbons (PAHs)
Derivatives of PAH
Multifunctional derivatives of PAH
Heterocyclic compounds
Derivatives of heterocyclics
Multifunctional derivatives of heterocyclic compounds

[a]Derivatives include acids, alcohols, aldehydes, esters, ketones, nitrates, and sulfonates.

Source: Adapted from Schuetzle (1988).

achieved by using specific solvents (or solvent mixtures) for the elution of compounds from chromatographic columns. Schuetzle and co-workers (1985) proposed that standard chemical compounds be selected for establishing reference points for the fractionation of diesel POM into nonpolar, moderately polar, and polar fractions by normal-phase HPLC. They proposed that the elution of 1-nitronaphthalene would define the end of the elution of nonpolar compounds and the beginning of the moderately polar fractions. In a similar way, 1,6-pyrene quinone would define the end of elution of moderately polar compounds and the beginning of the polar region.

For diesel engine emissions, ≈57% of the extracted organic mass is contained in the nonpolar fraction (Schuetzle, 1983). About 90% of this fraction consists of aliphatic hydrocarbons from approximately C_{14} to about C_{40}, with a carbon number maximum at C_{22} to C_{26} (Black and High, 1979; Pierson et al., 1983). Polycyclic aromatic hydrocarbons and alkyl-substituted PAH account for the remainder of the nonpolar mass.

The moderately polar fraction (≈9% w/w of extract) consists mainly of oxygenated PAH species and nitrated PAHs. The polar fraction (≈32% w/w of extract) is composed mainly of carboxylic and dicarboxylic acids of PAH, hydroxy-PAH, hydroxynitro-PAH, nitrated N-containing heterocyclic compounds, etc. (Schuetzle, 1983; Schuetzle et al., 1985).

Limited recovery studies have shown that there is little degradation or loss of diesel POM on the HPLC column. More than 90% of the mass and 70% to 100% of the Ames *S. typhimurium*-active material injected onto the column have been recovered (Schuetzle et al., 1985).

2.3.2.3.3. *Polycyclic aromatic hydrocarbons.* Particle-bound PAHs and their derivatives (mainly nitrated PAH) attracted considerable attention relatively early because of their mutagenic and, in some cases, carcinogenic properties (see, for example, National Research Council, 1982). The most widely used methods of PAH analysis included thin layer chromatography (TLC), capillary gas chromatography (GC), gas chromatography/mass spectrometry (GC/MS), and HPLC with ultraviolet or fluorescence detection (Levsen, 1988). Table 2-8 lists the PAHs and thioarenes identified and quantified by GC/MS in three LDD particulate matter extracts (Tong and Karasek, 1984). Data listed in this table reveal the presence of a large number of alkyl derivatives of PAH, which are sometimes more abundant than the parent PAH.

Table 2-9 compares the emission rates of several representative PAHs from HDD, LDD, and gasoline (with and without catalytic converter) engines.

2.3.2.3.4. *Nitrated polycyclic aromatic hydrocarbons.* Nitro-PAHs (nitroarenes) have been shown to be present in diesel particulate extracts, though in much lower concentration than the parent PAHs (Schuetzle et al., 1981, 1982; Paputa-Peck et al., 1983). Because many nitroarenes

Table 2-8. Polycyclic aromatic hydrocarbons identified and quantified in extracts of diesel particles

Compound[a,b]	Molecular weight	Concentration (ng/mg extract)[c,d]
Acenaphthylene	152	30
Trimethylnaphthalene	170	140-200
Fluorene	166	100-168
Dimethylbiphenyl	182	30-91
C_4-Naphthalene	184	285-351
Trimethylbiphenyl	196	50
Dibenzothiophene	184	129-246
Phenanthrene	178	2,186-4,883
Anthracene	178	155-356
Methyldibenzothiophene	198	520-772
Methylphenanthrene	192	2,028-2,768
Methylanthracene	192	517-1,522
Ethylphenanthrene	206	388-464
4H-Cyclopenta[def]phenanthrene	190	517-1,033
Ethyldibenzothiophene	212	151-179
2-Phenylnaphthalene	204	650-1,336
Dimethyl(phenanthrene/anthracene)	206	1,298-2,354
Fluoranthene	202	3,399-7,321
Benzo[def]dibenzothiophene	208	254-333
Benzacenaphthylene	202	791-1,643
Pyrene	202	3,532-8,002
Ethylmethyl(phenanthrene/anthracene)	220	590-717
Methyl(fluoranthene/pyrene)	216	1,548-2,412
Benzo[a]fluorene/benzo[b]fluorene	216	541-990
Benzo[b]naphtho[2,1-d]thiophene	234	30-53
Cyclopentapyrene	226	869-1,671
Benzo[ghi]fluoranthene	226	217-418
Benzonaphthothiophene	234	30-126
Benz[a]anthracene	228	463-1,076
Chrysene or triphenylene	228	657-1,529
1,2-Binapthyl	254	30-50
Methylbenz[a]anthracene	242	30-50
3-Methylchrysene	242	50-192
Phenyl(phenanthrene/anthracene)	254	210-559
Benzo[j]fluoranthene	252	492-1,367
Benzo[b]fluoranthene	252	421-1,090
Benzo[k]fluoranthene	252	91-289
Benzo[e]pyrene	252	487-946
Benzo[a]pyrene	252	208-558
Benzo[ah]anthracene	278	50-96
Indeno[1,2,3-[cd]pyrene	276	30-93
Benzo[ghi]perylene	276	443-1,050
Dibenzopyrene	302	136-254

[a]Compounds are arranged according to increasing gas chromatography retention times.
[b]Isomeric alkyl derivatives are not listed separately.
[c]Concentration range as found in the particulate extracts of three Volkswagen passenger cars.
[d]Soluble organic fractions accounted for 11.1%, 12.1%, and 14.7% of total particulate matter (w/w) for these three diesel samples.
Source: Tong and Karasek, 1984.

Table 2-9. Emission rates of particle-bound polycyclic aromatic hydrocarbons (PAHs) (in milligrams per kilometer) from HDD, LDD, and gasoline engines

PAH	HDD	LDD	Gasoline cars Noncatalyst	Gasoline cars Catalyst
Pyrene	17.6 (11)[a]	66 (42)[b]	45 (28)[c]	7 (4.4)[d]
Fluoranthene	27.2 (17)[a]	50 (31)[b]	32 (20)[c]	5 (3.1)[d]
Benzo[a]pyrene	<0.1 (0.06)[a]	1 (0.6)[d]	3.2 (2)[c]	0.4 (0.25)[d]
	2.3 (1.4)[e]	ND[b]		
Benzo[e]pyrene	0.24 (.15)[a]	3 (1.9)[d]	4.8 (3)[c]	0.4 (0.25)[d]

[a]From Westerholm et al. (1991).
[b]From Smith (1989), four-cycle FTP test, 1986 Mercedes Benz.
[c]From Alsberg et al. (1985).
[d]From Schuetzle and Frazier (1986).
[e]From Dietzman et al. (1980), averaged value for four different engines.

ND = None detected.

are potent direct-acting (e.g., without metabolic activation) mutagens in the Ames assay using *S. typhimurium* strains (Rosenkranz and Mermelstein, 1983), the analysis of nitro-PAHs in diesel POM attracted considerable attention in the early 1980s.

Numerous nitro-PAHs were identified in LDD particulate extracts using capillary GC with thermionic nitrogen-phosphorus detector (NPD) (Paputa-Peck et al., 1983). Positive isomer identification for 16 nitro-PAHs has been made utilizing the GC retention times of authentic standards and low- and high-resolution mass spectra as identification criteria. These include 1-nitropyrene; 2-methyl-1-nitronaphthalene; 4-nitrobiphenyl; 2-nitrofluorene; 9-nitroanthracene; 9-methyl-10-nitroanthracene; 2-nitroanthracene; 2-nitrophenanthrene; 1-methyl-9-nitroanthracene; 1-methyl-3-nitropyrene; 1-methyl-6-nitropyrene; 1-methyl-8-nitropyrene; 1,3-, 1,6-, and 1,8-dinitropyrene; and 6-nitrobenzo[a]pyrene. In addition, two nitrated heterocyclic compounds were identified, 5- and 8-nitroquinoline. Forty-five additional nitro-PAHs were tentatively identified in this diesel particulate extract (Paputa-Peck et al., 1983).

The concentration of nitro-PAHs adsorbed on diesel particles varies substantially from sample to sample. Usually 1-nitropyrene is the predominant component, and concentrations ranging from ≈7 to ≈165 µg/g of particles are reported (Levsen, 1988).

Table 2-10 gives the approximate concentrations of several more abundant nitro-PAHs in LDD particulate extracts.

2.3.2.3.5. *Oxygenated polycyclic aromatic hydrocarbons.* The moderately polar fraction of diesel particulate extract contains a variety of oxy-PAHs (in particular, aldehydes, ketones, quinones, and acid anhydrides) in much higher amounts than nitro-PAHs, which elute in the

Table 2-10. Concentrations of nitro-polycyclic aromatic hydrocarbons identified in a light-duty diesel (LDD) particulate extract

Nitro-PAH[a]	Concentration (µg/g of particles)
4-Nitrobiphenyl	2.2
2-Nitrofluorene	1.8
2-Nitroanthracene	4.4
9-Nitroanthracene	1.2
9-Nitrophenanthrene	1.0
3-Nitrophenanthrene	4.1
2-Methyl-1-nitroanthracene	8.3
1-Nitrofluoranthene	1.8
7-Nitrofluoranthene	0.7
3-Nitrofluoranthene	4.4
8-Nitrofluoranthene	0.8
1-Nitropyrene	18.9; 75[b]
6-Nitrobenzo[a]pyrene	2.5
1,3-Dinitropyrene[b]	0.30
1,6-Dinitropyrene[b]	0.40
1,8-Dinitropyrene[b]	0.53
2,7-Dinitrofluorene[c]	4.2; 6.0
2,7-Dinitro-9-fluorenone[c]	8.6; 3.0

[a]From Campbell and Lee (1984) unless noted otherwise. Concentrations recalculated from µg/g of extract to µg/g of particles using a value of 44% for extractable material (w/w).
[b]From Paputa-Peck et al. (1983).
[c]From Schuetzle (1983).

same fraction. Oxy-PAHs are nonmutagenic or very weakly mutagenic; this explains the relatively low interest in this group of compounds. The most detailed study of oxy-PAHs was published by Schuetzle et al. (1981), who identified more than 100 compounds. A large number of oxy-PAHs in the molecular weight range of 182 to 272 were also identified by Tong et al. (1984). The main components identified by Tong and co-workers in particulate matter extracts of three LDD cars (Volkswagens) were 9-fluorenone, anthraquinone, 4H-cyclopenta[*def*]phenanthrene-4-one, 9-phenanthrene aldehyde, benzo[*de*]anthracene-7-one, and benzo[*cd*]pyrene-6-one. These components are present at concentrations of 30 to 300 µg/g particles. Some of these oxy-PAHs are formed during sampling (Levsen, 1988).

2.3.2.3.6. *Polar polycyclic aromatic hydrocarbon derivatives.* According to Schuetzle et al. (1985), although 65% to 75% of the directly acting mutagenicity (as tested by Ames *S. typhimurium* assay) for LDD particulate extracts is associated with the fraction of moderate polarity, more than 65% of the mutagenic activity for HDD particulate extract is concentrated in

the most polar fraction. However, because of the serious analytical difficulties, only preliminary data exist on the identification of compounds that are responsible for the mutagenic activity of this fraction (so-called "polar mutagens"). Schuetzle and co-workers (1985) employed the concept of "bioassay directed chemical analysis" (see Section 2.6) for the isolation and identification of polar PAH derivatives from the extracts of HDD particulate matter (National Institute of Standards and Technology [NIST] standard reference material SRM 1650). Several hydroxynitro-PAHs, hydroxy-PAHs, and nitrated heterocyclic compounds were tentatively identified in the polar fraction. It has to be noted, however, that NIST SRM 1650 was not intended to be representative of HDD engines but was a material made available to investigators for the purpose of methods development.

In another study (Bayona et al., 1988), the polar HPLC fractions of the same NIST SRM 1650 were analyzed by fused silica capillary GC with low- and high-resolution mass MS, using electron impact (EI) and negative ion chemical ionization (NICI) techniques. In addition, direct-probe EI and NICI-MS analyses were performed. More than 80 polycyclic aromatic compounds (PAC) belonging to several different chemical classes (anhydrides, carboxaldehydes, diazaarenes, cyclic imides, hydroxynitro-PAH, nitroaza-PAC, nitrolactones, and quinones) were tentatively identified. Ten were positively identified by comparison of retention times with authentic standards. Among them, phenazine and phthalic anhydride were positively identified for the first time in diesel exhaust particles. In addition, cyclic imides and their alkylated derivatives were tentatively identified.

2.3.3. Gaseous-/Particulate-Phase Emission Partitioning of Polycyclic Aromatic Hydrocarbons

The distribution of the emissions between the gaseous and particulate phases is determined by the vapor pressure of the individual species, by the amount and type of the particulate matter present (adsorption surface available), and by the temperature (Ligocki and Pankow, 1989). Table 2-11 gives the vapor pressures at 25°C of some representative PAHs ranging from naphthalene to benzo[a]pyrene.

The factor of $\approx 10^7$ in the range of vapor pressures is reflected in the fact that, at equilibrium at ambient temperature, naphthalene exists almost entirely in the gas phase, whereas B[a]P, other five-ring PAHs, and higher-ring PAHs are predominantly adsorbed on particles. The intermediate three- and four-ring PAHs are distributed between the two phases.

However, the vapor pressures of these intermediate PAHs can be significantly reduced by their adsorption on various types of surfaces. Because of this phenomenon, the amount and type

Table 2-11. Vapor pressures at 25°C for a series of polycyclic aromatic hydrocarbons[a] (PAHs)

PAH	Vapor pressure at 298 K (torr)
Naphthalene	8.0×10^{-2}
Acenaphthylene	6.7×10^{-3}
Acenaphthene	2.2×10^{-3}
Fluorene	6.0×10^{-4}
Phenanthrene	1.2×10^{-4}
Anthracene	6.0×10^{-6}
Fluoranthrene	9.2×10^{-6}
Pyrene	4.5×10^{-6}
Benzo[a]anthracene	2.1×10^{-7}
Benzo[a]pyrene	5.6×10^{-9}
Chrysene[b]	6.4×10^{-9}

[a]Sonnefeld et al. (1983), except as indicated.
[b]Yamasaki et al. (1984).

of particulate matter present play an important role, together with temperature, in the vapor-particle partitioning of semivolatile organic compounds (SOC).

The measurements of gas/particulate phase distribution are often accomplished by using a high-volume filter followed by an adsorbent such as polyurethane foam (PUF), Tenax, or XAD-2 (Cautreels and Van Cauwenberghe, 1978; Thrane and Mikalsen, 1981; Yamasaki et al., 1982). However, the pressure drop behind a high-volume filter or cascade impactor contributes to volatilization of the three- to five-ring PAHs, to a degree reflecting their vapor pressures. The magnitude of this "blow-off" artifact depends on a number of factors, including sampling temperature and the volume of air sampled (Van Vaeck et al., 1984; Coutant et al., 1988). Despite these problems from volatilization, measurements with the high-volume filters followed by a solid adsorbent have provided most estimates of vapor-particle partitioning of SOC in ambient air, as well as insights into the factors influencing SOC adsorption onto aerosols.

Average distributions of PAH between high-volume filter and PUF plugs (positioned downstream of the filter) in samples collected in a heavily traveled roadway tunnel (Baltimore Harbor Tunnel) are shown in Figure 2-2. As discussed in the preceding text, the "blow-off" from the filter precludes detailed quantitative interpretation. However, it can be seen from this figure that significant fractions of phenanthrene, anthracene, and their alkylated derivatives, along with fluoranthene and pyrene, exist in the gas phase. No PAHs less volatile than pyrene were
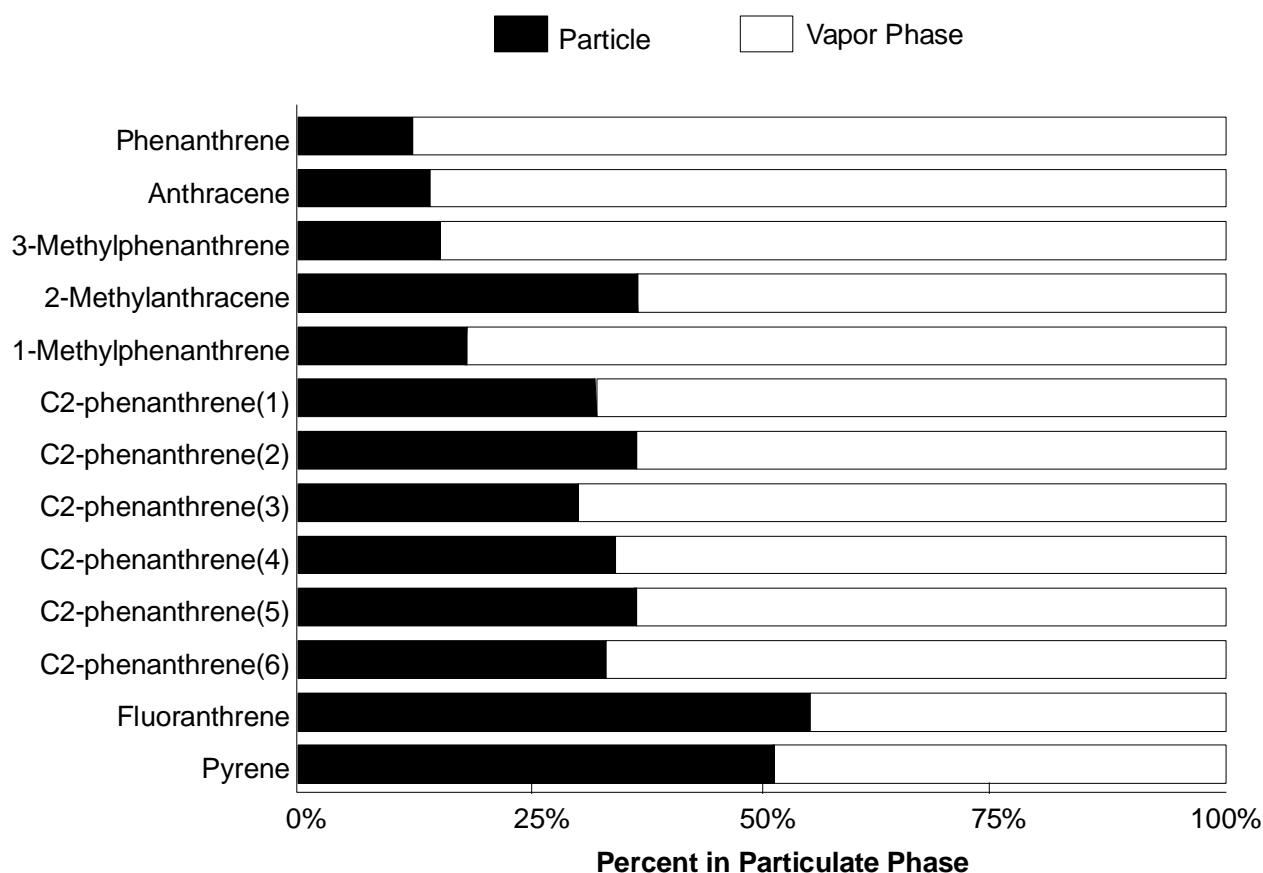
Figure 2-2. Vapor/particle phase polycyclic aromatic hydrocarbon distribution in samples collected in Baltimore Harbor Tunnel.

Source: Benner et al. (1989).

observed in any of the PUF samples. Comparison of the observed vapor-to-particle PAH ratios and those calculated based on the relationship derived by Yamasaki and co-workers (1982) generally agreed within a factor of 2 (Benner et al., 1989).

2.4. ATMOSPHERIC TRANSFORMATIONS OF PRIMARY DIESEL EMISSIONS

2.4.1. Long-Range Transport and Fate of Primary Diesel Emissions

Once released into the atmosphere, primary diesel emissions (or any other direct emissions) are subject to dispersion and transport and, at the same time, to various physical and chemical processes that determine their ultimate environmental fate. The role of the atmosphere may be compared in some way with that of a giant chemical reactor in which materials of varying reactivity are mixed together, subjected to chemical and/or physical processes, and finally removed (Schroeder and Lane, 1988). The main features of the atmospheric cycle for primary

diesel emissions, beginning with emission and ending with deposition to the Earth's surface, are shown in Figure 2-3.

Initial mixing describes the physical processes that act on pollutants immediately after their release from an emission source. The dilution of diesel exhaust under roadway conditions is an important factor to consider; whereas a dilution factor of 10 is typical of many dilution tunnels used in dynamometer studies of automobile exhaust, a dilution factor of $\approx 10^3$ is more realistic under roadway conditions. This discrepancy leads to slightly different particle size distributions under real driving conditions than those predicted from laboratory data (Kittelson and Dolan, 1980); for example, because of slower coagulation processes, more particles in the Aitken nuclei range ($\leq 0.08\ \mu m$ diameter) may be expected under typical roadway conditions.

Diffusion and transport processes occur simultaneously in the atmosphere and account for the dispersion of emissions. The actual distance traveled by gaseous- and particulate-phase
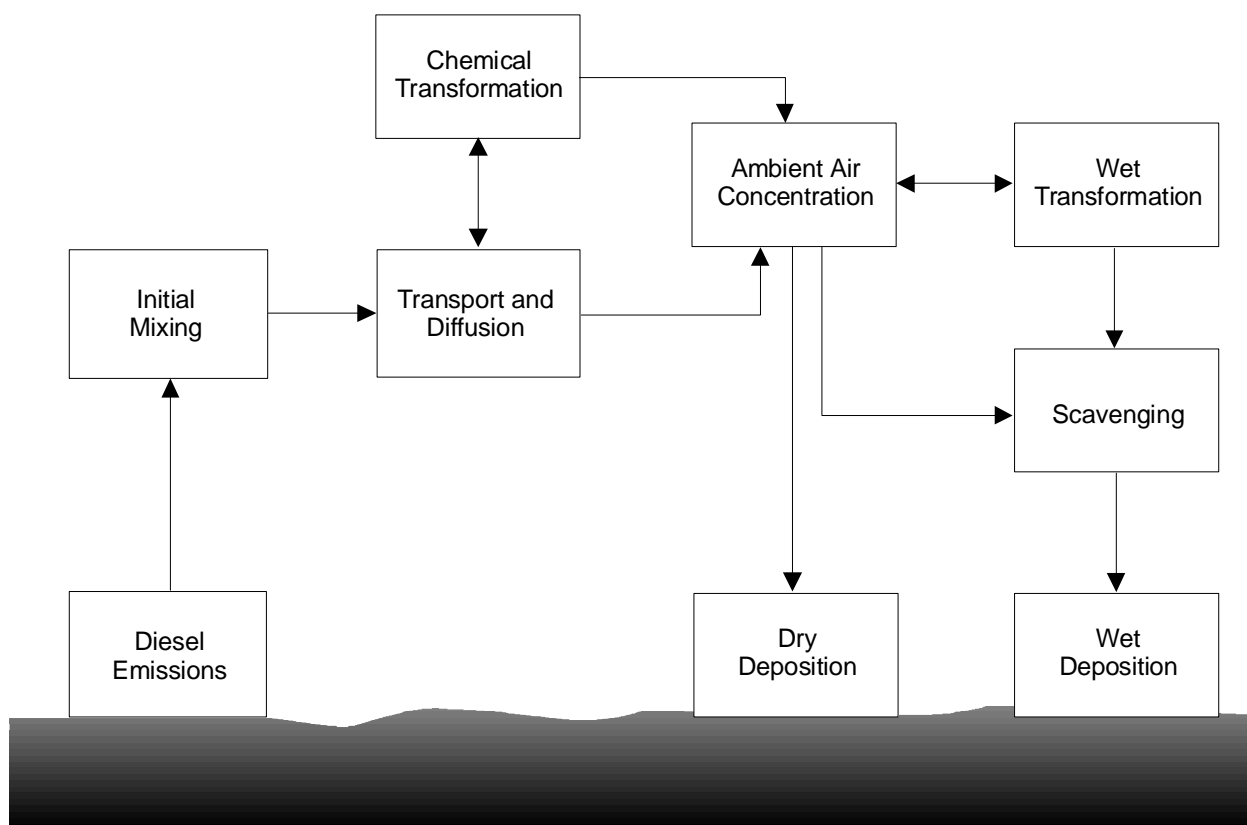
Figure 2-3. Diesel-derived pollutants: emission-to-deposition atmospheric cycle.

Source: Schroeder and Lane (1988).

pollutants depends on the amount of time a specific pollutant resides in the atmosphere and is available for dispersion (Schroeder and Lane, 1988). As primary diesel emissions are a very complex mixture containing thousands of organic and inorganic constituents in the gas and particulate phases that have different chemical reactivities, they are removed by dry and wet deposition processes at different rates. The more reactive compounds with short lifetimes will be removed from the atmosphere relatively quickly, whereas more stable pollutants can be transported over greater distances. Clearly, a knowledge of the atmospheric loss processes and lifetimes for automotive emissions is important, because these lifetimes determine the geographic extent of the influence of these emissions.

Anthropogenic pollutants can travel through the atmosphere over long distances. In particular, the long-range transport of SO_2 and its transformation to $SO_4^=$ have been studied extensively (Galloway and Whelpdale, 1980; Lowenthal and Rahn, 1985). The organic pollutants, particularly those adsorbed on carbonaceous particles, are also subjected to long-range transport. Organic compounds, such as PAHs, adsorbed on diesel particulate matter are generally more resistant to atmospheric reactions than those in the gas phase. In addition, particles of smaller diameter (<1 µm), such as diesel particulate matter (Figure 2-1), are removed less efficiently than larger particles by wet and dry deposition and thus have longer atmospheric residence times.

It has been reported (Laflamme and Hites, 1978; Hites et al., 1980) that PAHs and their alkyl homologs are distributed in sediments throughout the world and that the PAH patterns are similar to each other and to air particulate matter for most of the locations studied. Furthermore, the quantities of PAHs increase with proximity to urban areas. This suggests anthropogenic combustion sources and long-range atmospheric transport of PAHs.

Evidence for long-range transport of PAHs was also reported from the recent measurements of PAHs in Siskiwit Lake, located on a wilderness island in northern Lake Superior (McVeety and Hites, 1988). Because of the lake's remote location, PAHs found in this lake are likely to have originated from atmospheric transport.

Earlier studies by Bjørseth and co-workers (Bjørseth and Olufsen, 1983) showed that PAHs are transported from Great Britain and the European continent to remote locations in Norway and Sweden. The specific sources of PAH emissions could not be identified, however. The authors speculated that combustion engines were not the major sources, because the amounts of B[*a*]P found in the samples collected in Norway and Sweden were higher than could be accounted for from gasoline and diesel fuel consumption in Great Britain and because the coronene/B[*a*]P ratios in the samples were lower than those usually found in gasoline and diesel exhaust. However, because of the lack of PAH profiles specifically for combustion engines (or, as a matter of fact, any other specific tracer), the relative contribution of gasoline and diesel vehicle exhausts to long-range transport of organics could not be determined.

2.4.2. Chemical Transformations

2.4.2.1. *Gas-Phase Reactions*

The following chemical processes contribute to the removal of gas-phase compounds from the atmosphere (Atkinson, 1988):

- Photolysis during daylight hours;

- Reaction with hydroxyl (OH) radicals during daylight hours;

- Reaction with ozone (O_3) during daytime and nighttime;

- Reaction with hydroperoxyl (HO_2) radicals, typically during late daytime and early nighttime hours;

- Reaction with gaseous nitrate (NO_3) radicals during nighttime hours;

- Reaction with dinitrogen pentoxide (N_2O_5) during nighttime hours;

- Reaction with NO_2 during daytime and nighttime hours; and

- Reaction with gaseous nitric acid (HNO_3) and other species such as nitrous (HNO_2) acid and sulfuric acid (H_2SO_4).

It has been shown (Atkinson et al., 1990) that the N_2O_5 reactions with PAHs proceed by initial NO_3 addition to form an NO_3-PAH adduct, which either dissociates back to reactants or reacts exclusively with NO_2 to form nitroarenes and other products. Because under atmospheric conditions, where N_2O_5, NO_3 radicals, and NO_2 are in equilibrium, these reactions are kinetically equivalent to a reaction with N_2O_5 with an effective N_2O_5 reaction rate constant, we will further refer to these reactions as N_2O_5 reactions.

The reactive gaseous species, such as OH radicals, NO_3 radicals, HO_2 radicals, and ozone, are present in the atmosphere either during the daytime (OH radicals) or nighttime (N_2O_5 and NO_3 radicals) hours or both time periods (ozone, NO_2). For the routes of formations of these species and their concentrations in the troposphere, see Finlayson-Pitts and Pitts (1986).

Table 2-12 gives the calculated atmospheric lifetimes for some selected compounds present in automotive gas-phase emissions as the result of known tropospheric chemical removal reactions (Atkinson, 1988). These lifetimes (i.e., the time for the compound to decay to 1/e or

Table 2-12. Calculated atmospheric lifetimes for gas-phase reactions of selected compounds present in automotive emissions with atmospherically important reactive species

Compound	Atmospheric lifetime resulting from reaction with				
	OH[a]	O_3[b]	NO_3[c]	HO_2[d]	hv[e]
NO_2	2 days	12 h	1 h	2 h	2 min
NO	4 days	1 min	3 min	20 min	—
HNO_3	180 days	—	—	—	—
SO_2	26 days	>200 years	$>4 \times 10^4$ years	>600 years	—
NH_3	140 days	—	—	—	—
Propane	19 days	>7,000 years	—	—	—
n-Butane	9 days	>4,500 years	9 years	—	—
n-Octane	3 days	—	3 years	—	—
Ethylene	3 days	9 days	3 years	—	—
Propylene	11 h	1.5 days	15 days	—	—
Acetylene	30 days	6 years	>14 years	—	—
Formaldehyde	3 days	$>2 \times 10^4$ years	210 days	23 days	4 h
Acetaldehyde	1 day	>7 years	50 days	—	60 h
Benzaldehyde	2 days	—	60 days	—	—
Acrolein	1 day	60 days	—	—	—
Formic acid	50 days	—	—	—	—
Benzene	18 days	600 years	>16 years	—	—
Toluene	4 days	300 years	9 years	—	—
m-Xylene	11 h	75 years	2 years	—	—
Phenol	10 h	—	20 min	—	—
Naphthalene	1 day	>80 days	—[f]	—	—
2-Methylnaphthalene	5 h	>40 days	—[f]	—	—
2,3-Dimethylnaphthalene	4 h	>40 days	—[f]	—	—
Acenaphthene	2 h	>30 days	≈3 h	—	—
Acenaphthylene	2 h	≈50 min	13 min	—	—
Phenanthrene	9 h	—	—	—	—
Anthracene	2 h	—	—	—	—
Fluoranthene[g]	6 h	—	—[f]	—	—
Pyrene[g]	6 h	—	—[f]	—	—

[a]For 12-h average concentration of OH radical of 1×10^6 molecule/cm^3.
[b]For 24-h average O_3 concentration of 7×10^{11} molecule/cm^3.
[c]For 12-h average NO_3 concentration of 2×10^8 molecule/cm^3.
[d]For 12-h average HO_2 concentration of 10^8 molecule/cm^3.
[e]For solar zenith angle of 0°.
[f]Lifetimes due to gas-phase reactions with a 12-h average concentration of N_2O_5 of 2×10^{10} molecule/cm^3 are: naphthalene, ≈80 days; 2-methylnaphthalene, ≈35 days; 2,3-dimethylnaphthalene, ≈20 days; fluoranthene, ≈64 days; and pyrene, ≈20 days.
[g]Lifetimes calculated from kinetic data given in Atkinson et al. (1990).

Source: Atkinson (1988) unless noted otherwise.

37% of its original concentration) are calculated from the corresponding measured reaction rate constants and the average ambient concentration of the tropospheric species involved.

Although the individual rate constants are known to a reasonable degree of accuracy (in general, to within a factor of 2), the tropospheric concentrations of these key reactive species are much more uncertain. For example, the ambient concentrations of OH radicals at any given time and/or location are uncertain to a factor of at least 5, and more likely 10 (Atkinson, 1988). The tropospheric diurnally and annually averaged OH radical concentrations are more certain, to possibly a factor of 2. For this reason, the calculated lifetimes listed in Table 2-12 are approximate only and are valid for those reactive species concentrations listed in the table footnotes. However, these data permit estimation of the contribution of each of these atmospheric reactions to the overall rates of removal of most pollutants from the atmosphere.

As can be seen from Table 2-12, the major atmospheric loss process for most of the automotive emission constituents listed is by daytime reaction with OH radicals. For some pollutants photolysis, reactions with ozone, and reactions with NO_3 radicals during nighttime hours are also important removal routes.

The atmospheric lifetimes do not take into consideration the potential chemical or biological importance of the products of these various reactions. For example, the reaction of gas-phase PAHs with N_2O_5 appears to be of minor significance as a PAH loss process but, as will be discussed in subsequent sections, is more important as a route of formation of mutagenic nitro-PAHs.

2.4.2.1.1. *Reactions of nitrogen oxides.* Only the major atmospheric reactions of NO_x are considered here; for detailed discussion of the chemistry of these important species, see Finlayson-Pitts and Pitts (1986).

Oxides of nitrogen emitted by diesel engines include mainly NO, with lesser amounts of NO_2. Nitric oxide is easily oxidized to NO_2 in reactions with HO_2 radicals and alkylperoxy radicals (the reaction of NO with O_2 is too slow at typical ambient concentrations of NO). In addition, NO reacts rapidly (Table 2-3) with ozone via Reaction 1:

$$NO + O_3 \rightarrow NO_2 + O_2 \tag{1}$$

Nitrogen dioxide is photolyzed rapidly at wavelengths of <430 nm:

$$NO_2 + h\nu \rightarrow NO + O(^3P) \tag{2}$$

The oxygen atom produced in this reaction reacts with O_2, forming ozone:

$$O_2 + O(^3P) \rightarrow O_3 \tag{3}$$

The photolysis of NO_2 is the only known significant anthropogenic source of ozone in the ambient air and is produced via Reactions 2 and 3. With this series of reactions, NO, NO_2, and O_3 are in a photostationary state:

$$NO + O_3 \longrightarrow NO_2 + O_2$$
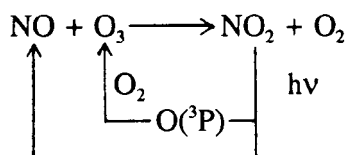
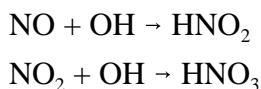with

$$[O_3] = \frac{k_2[NO_2]}{k_1[NO]}$$

where k_1 and k_2 are the rate constants for Reactions 1 and 2, respectively, and brackets signify concentrations. This photostationary state is strongly affected by NO-to-NO$_2$ conversions caused by reactions involving organic compounds.

The important atmospheric reactions of NO$_2$ also include formation of NO$_3$ radicals and N$_2$O$_5$:

$$NO_2 + O_3 \rightarrow NO_3 + O_2$$

$$NO_2 + NO_3 \overset{M}{\underset{\leftarrow}{\rightarrow}} N_2O_5$$
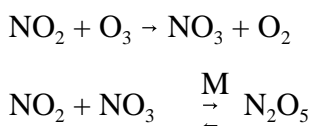
with N$_2$O$_5$ being in equilibrium with NO$_2$ and NO$_3$ radicals.

The other important atmospheric reactions of NO and NO$_2$ include nitrous and nitric acid formation, respectively, by reaction with OH radicals:

$$NO + OH \rightarrow HNO_2$$
$$NO_2 + OH \rightarrow HNO_3$$

2.4.2.1.2. *Reactions of sulfur dioxide.* Reaction with OH radical is the dominant SO$_2$ atmospheric gas-phase reaction process (Stockwell and Calvert, 1983):

$$SO_2 + OH \rightarrow HSO_3$$

followed by the formation of HO$_2$ radicals and H$_2$SO$_4$:

$$HSO_3 + O_2 \rightarrow HO_2 + SO_3$$

$$\downarrow \quad H_2O$$
$$H_2SO_4$$
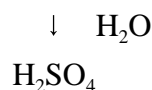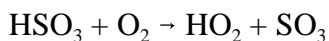
Because SO$_2$ is soluble in water, it undergoes scavenging by fog, cloud water, and raindrops. In aqueous systems, SO$_2$ is readily oxidized to sulfate (Calvert and Stockwell, 1983).

2.4.2.1.3. *Reactions of alkanes.* Only a brief overview of the most important atmospheric reactions of alkanes is presented here; for detailed discussion, consult Finlayson-Pitts and Pitts (1986) and Atkinson (1988, 1990).

Under atmospheric conditions, alkanes react with OH radicals during the daytime and with NO_3 radicals during the nighttime:

$$RH + OH \rightarrow R^{\bullet} + H_2O$$
$$RH + NO_3 \rightarrow R^{\bullet} + HNO_3$$
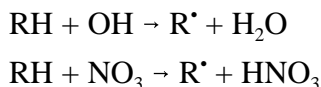
Alkyl radical $R^{\bullet}$ reacts with O_2, forming an alkylperoxy radical:

$$R^{\bullet} + O_2 \xrightarrow{M} RO_2^{\bullet}$$
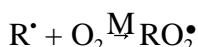
which, under polluted urban atmospheric conditions, reacts predominantly with NO by two pathways: (a) oxidation of NO to NO_2 and formation of alkoxy radical ($RO^{\bullet}$), the only significant path for the smaller ($\leq C_4$) radicals and (b) the addition reaction to form stable alkyl nitrates, the significant pathway for larger alkyl peroxy radicals:

$$RO_2^{\bullet} + NO \begin{array}{c} \xrightarrow{\,a\,} RO^{\bullet} + NO_2 \\ \\ \xrightarrow{\,b\,} RONO_2 \end{array}$$
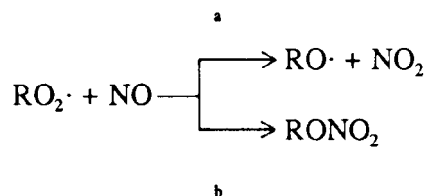
Alkoxy radical ($RO^{\bullet}$) reacts essentially by three routes: (a) with O_2, by abstraction of H atom from the neighboring carbon and formation of stable carbonyl compound and HO_2 radical; (b) unimolecular decomposition to form stable carbonyl compounds and free radicals, which will react further, probably by analogous routes as discussed for alkyl radicals in the preceding text; and (c) unimolecular isomerization by 1,4- or 1,5-hydrogen shift (if a hydrogen atom in appropriate position is available), forming α- or β-substituted alkyl radical, which will react with O_2 as discussed in the preceding text.

For example, for 2-pentoxy radical:

$$CH_3CH_2CH_2CHCH_3$$
$$|$$
$$O^{\bullet}$$

a. with O_2: $CH_3CH_2CH_2CCH_3 + HO_2$ (with carbonyl O)

b. $CH_3CHO + CH_3CH_2CH_2^{\bullet}$

c. 1,5-H Shift: $^{\bullet}CH_2CH_2CH_2CHCH_3$ with OH
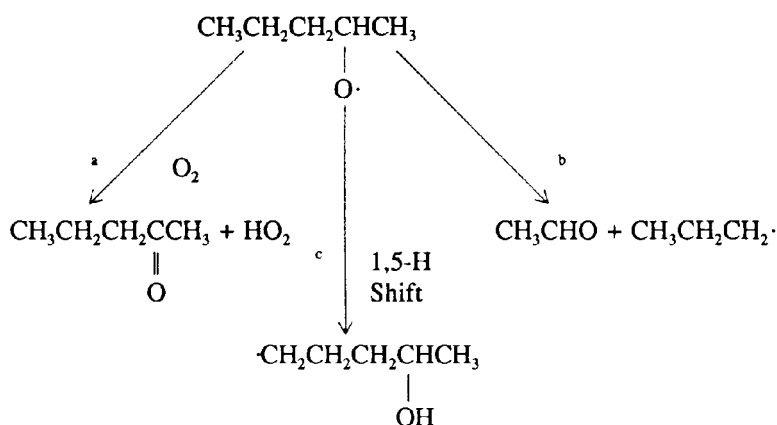
For the simplest alkoxy radicals, reaction with O_2 (pathway a) is predominant. For larger radicals, however, isomerization (c) and decomposition (b) may become significant, the relative importance of these two pathways depending on the structure of the radical. In all three cases, free radicals are produced, which then will carry on the chain reactions. The first-generation products include aldehydes, ketones, and alkyl nitrates, which can react further under atmospheric conditions.

2.4.2.1.4. *Reactions of alkene.* Lower molecular weight alkenes, such as ethylene, propylene, and isomeric butenes, are present in exhaust from gasoline and (although in lower amount) diesel engines (see Table 2-2). Gas-phase alkenes are removed from the troposphere by reaction with OH radicals, NO_3 radicals, and O_3 (Finlayson-Pitts and Pitts, 1986; Atkinson, 1988; Atkinson and Carter, 1984). Reactions with OH radicals are rapid (see Table 2-13) and proceed by OH radical addition to the double bond.

Because the OH-olefin adduct is essentially an alkyl radical, it reacts further in a manner similar to alkyl radicals formed from the reaction of alkanes with OH radicals (e.g., by the addition of O_2 followed by reaction with NO). For example, for radical (a):
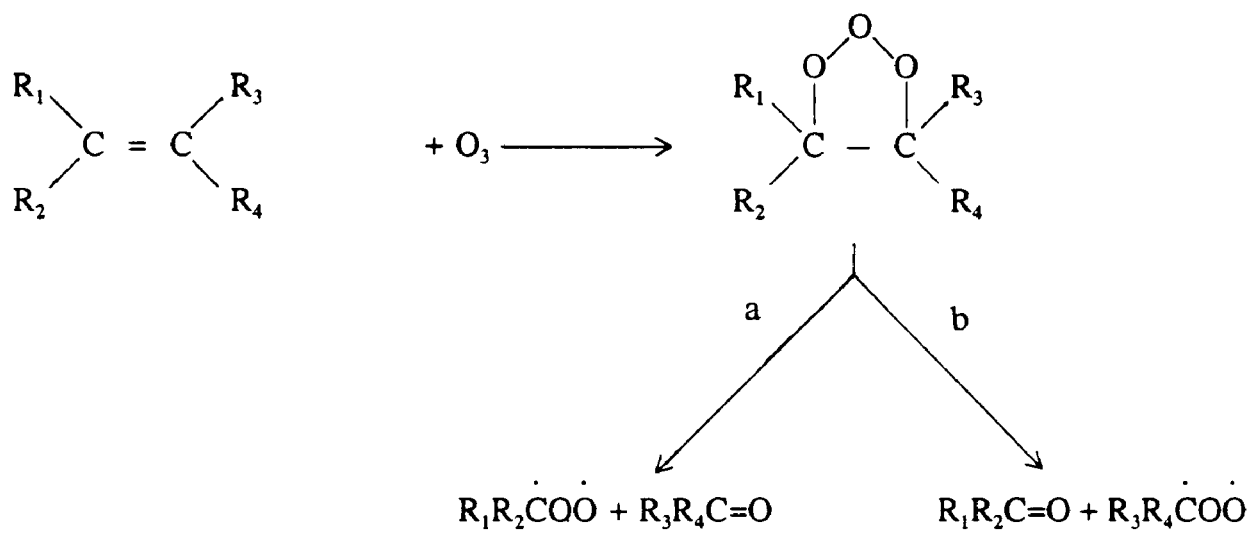
$$CH_3\dot{C}HCH_2OH + O_2 \xrightarrow[\quad NO \quad]{\quad \quad} CH_3\overset{O\cdot}{\underset{|}{C}}HCH_2OH$$

$$\downarrow NO_2$$
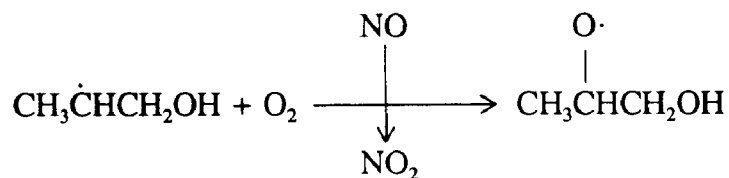
Table 2-3). Similar to the OH radical reaction, this reaction proceeds through NO_3 radical addition to the double bond, followed by reaction with O_2 (Finlayson-Pitts and Pitts, 1986; Atkinson, 1988). Carbonyl compounds are formed as major products, but minor products (possibly dinitrates) are not well defined (Atkinson, 1988).

The reactions of alkenes with ozone compete with the daytime OH radical reaction (Table 2-3). These reactions proceed by addition to the double bond, followed by rapid decomposition of so-called "ozonide" or "molozonide" into a carbonyl compound and an energy-rich biradical:

Table 2-13. Summary of the nitroarenes produced from the gas-phase hydroxyl (OH) radical-initiated and dinitrogen pentoxide (N_2O_5) reactions and electrophilic nitration of polycyclic aromatic hydrocarbons (PAHs)

| PAH	Position of nitration (yield) in reaction with		Position of electrophilic nitration
	OH	N_2O_5	
Naphthalene	1- (0.3%); 2- (0.3%)	1- (17%); 2- (7%)	1->2-
1-Methylnaphthalene	5->4-≥6-≥3-≥7-≈2->8- Total yield (≈0.4%)	3->5-≥4-≥8-≈6->7-≥2- Total yield (≈30%)	4->2->5->8->7-≈3->6-
2-Methylnaphthalene	5->6-≈7-≈4-≈8->3->1- Total yield (≈0.2%)	4->1-≈5-≥8-≈3-≈7-≈6- Total yield (≈30%)	1->8->4->6->5->3->7-
Acenaphthylene	4- (2%)	None observed	1-
Acenaphthene	5->3->4- Total yield (≈0.2%)	4- (40%); 3- (≈2%); 5- (≈2%)[a]	3-; 5-
Biphenyl	3- (5%)	No reaction observed	2-; 4-
Phenanthrene	Two isomers (not 9-nitrophenanthrene) Total yield (≤0.1%)	Four isomers (including 9-nitrophenanthrene) Total yield (<1%)	9->3-; 2-; 1-
Anthracene	1-; 2- Total yield (≈0.2%)	1-; 2- Total yield (<2%)	9-
Fluoranthene	2- (3%); 7- (~0.15%); 8- (≈0.15%)	2-(≈25-30%)	3->8->7->1-
Pyrene	2- (≈0.25%); 4- (≈0.045%)	4-; 2- Total yield (<1%)	1-
Acephenanthrylene	Two isomers (not 4- or 5-nitro-) Total yield (≈0.1%)	None observed	4-; 5-

[a]Concurrent NO_3 radical reaction will dominate over N_2O_5 reaction in ambient air.

The reaction of an alkene with ozone forming the molozonide, which decomposes via pathways (a) and (b):

$$R_1R_2\dot{C}O\dot{O} + R_3R_4C{=}O \qquad\qquad R_1R_2C{=}O + R_3R_4\dot{C}O\dot{O}$$

The importance of pathways (a) and (b) is assumed to be equal (Atkinson and Carter, 1984).

The major uncertainty concerns the atmospheric fate of the energy-rich intermediate, the so-called "Criegee biradical." It is believed that some of the Criegee intermediates contain sufficient excess energy to spontaneously decompose. The remaining "thermalized" species are expected to react in the atmosphere with NO, NO_2, SO_2, H_2O vapor, CO, and carbonyl compounds, although the rate constants and mechanisms of these reactions are uncertain (Finlayson-Pitts and Pitts, 1986).

2.4.2.1.5. *Reactions of oxygen-containing organics.* Diesel and gasoline vehicle exhausts contain aldehydes and carboxylic acids. The major loss processes for aldehydes involve photolysis and reaction with OH radicals (see Table 2-12). Photolysis is an important loss process for formaldehyde, forming H atom and HCO radical in the first step:
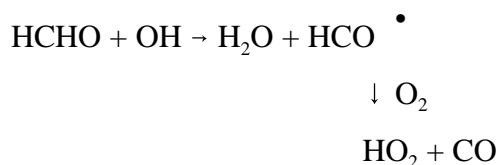
$$HCHO + h\nu \longrightarrow \begin{cases} H + HCO \\ H_2 + CO \end{cases}$$
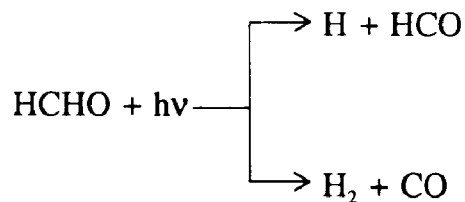
The rapid reaction of H atom and HCO radical with O_2 produces HO_2 radicals:
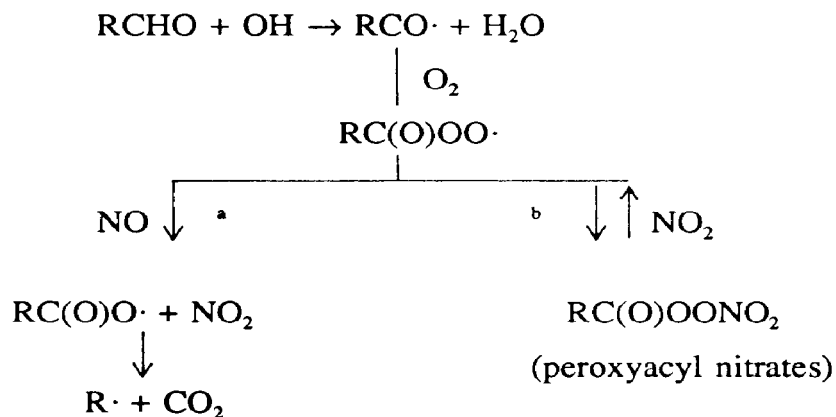
$$H + O_2 \rightarrow HO_2$$

$$HCO + O_2 \rightarrow HO_2 + CO$$
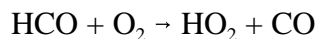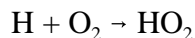
The higher aldehydes also photodissociate, ultimately yielding HO_2 radicals.

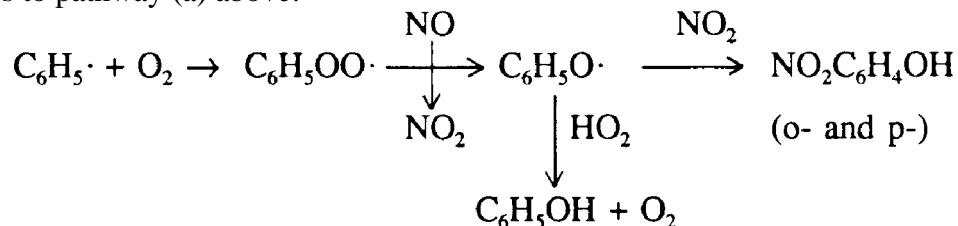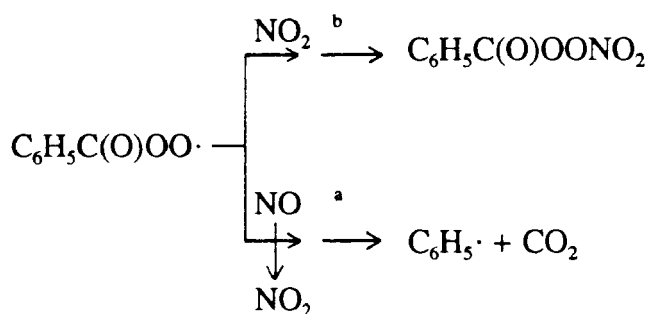The OH radical reaction with formaldehyde yields CO and HO_2:

$$HCHO + OH \rightarrow H_2O + HCO\,\overset{\bullet}{}$$
$$\downarrow O_2$$
$$HO_2 + CO$$

For higher aldehydes, the RCO radicals initially formed add O_2 to yield acylperoxy radical, which can react further with NO (pathway a) and NO_2 (pathway b):

$$RCHO + OH \rightarrow RCO\cdot + H_2O$$
$$\big| \; O_2$$
$$RC(O)OO\cdot$$

NO $\downarrow$ ᵃ   ᵇ $\downarrow\uparrow$ NO_2

$$RC(O)O\cdot + NO_2 \qquad\qquad RC(O)OONO_2$$
$$\downarrow \qquad\qquad\qquad\quad \text{(peroxyacyl nitrates)}$$
$$R\cdot + CO_2$$

Acetaldehyde forms peroxyacetyl nitrate (PAN), which has been shown to be a direct-acting mutagen toward Ames *S. typhimurium* strain TA100 (Kleindienst et al., 1985) and is phytotoxic.

Benzaldehyde, the simplest aromatic aldehyde, forms peroxybenzoyl nitrate by the series of reactions analogous to pathway (b) above and nitrophenols as a result of the reaction with NO, analogous to pathway (a) above:

$$C_6H_5\cdot + O_2 \rightarrow C_6H_5OO\cdot \xrightarrow{\;NO\;} C_6H_5O\cdot \xrightarrow{\;NO_2\;} NO_2C_6H_4OH$$
$$\downarrow NO_2 \qquad \big| HO_2 \qquad\quad \text{(o- and p-)}$$
$$\downarrow$$
$$C_6H_5OH + O_2$$

Carboxylic acids react with OH radicals under atmospheric conditions (Table 2-3). For formic acid, hydrogen atoms are produced (Atkinson, 1988):

$$HC(O)OH + OH \rightarrow H_2O + CO_2 + H$$
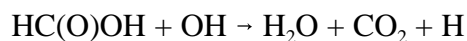
For the higher carboxylic acids, reaction products are currently unknown.

2.4.2.1.6. *Reactions of monocyclic aromatic compounds.* The monocyclic aromatic compounds are removed from the atmosphere solely by reactions with OH radicals (see Table 2-3). These reactions proceed by two pathways (Finlayson-Pitts and Pitts, 1986; Atkinson, 1988):

   (a)   a major pathway by OH radical addition to the aromatic ring, and

   (b)   a minor pathway by H atom abstraction, either from the aromatic ring (in the case of benzene) or from an alkyl group (in the case of alkyl-substituted aromatics). This latter pathway leads to the formation of aromatic aldehydes and is analogous to OH radical/reaction of alkanes.

For example, for toluene:
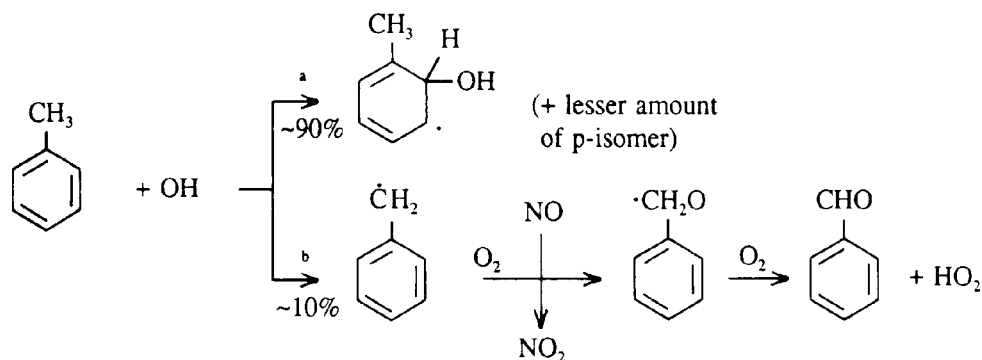
The products arising from the OH radical addition pathway (a) are not well known. Reaction with O_2, again occurring by two pathways, is expected to predominate:
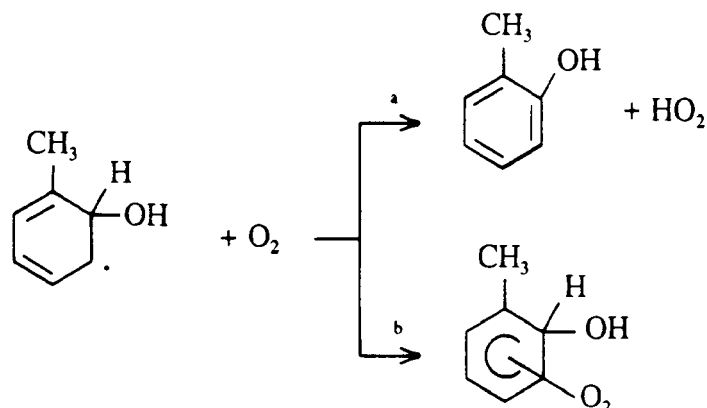
Pathway (a) yields phenolic compounds and, for toluene, accounts for $\approx 20\%$ of the overall reaction yield (Atkinson, 1988). The major reactions involve ring cleavage (opening), leading to a variety of bifunctional products (Finlayson-Pitts and Pitts, 1986).

For phenolic compounds, in addition to OH radical reaction (proceeding mainly by initial OH radical addition to the ring), the NO_3 radical reaction that yields nitrophenols appears to be important (Atkinson, 1988):
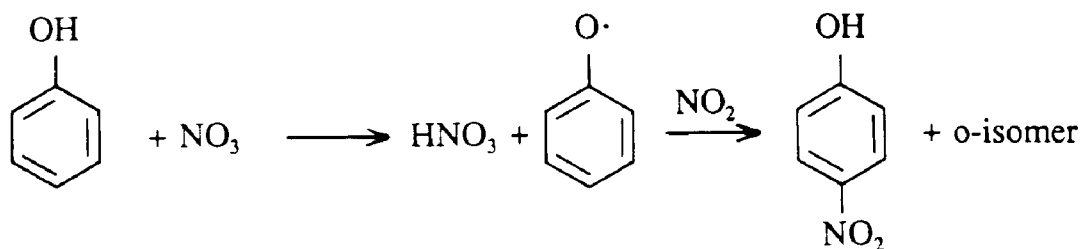

2.4.2.1.7. ***Reactions of polycyclic aromatic compounds.*** As discussed in Section 2.3.4, two- to four-ring PAHs emitted from diesel and spark-ignition engines are distributed between gas and particle phases. For those PAHs present in the gas phase, the reaction with OH radical is predominant, leading to atmospheric lifetimes of a few hours or less (see Table 2-12). The nighttime gas-phase reaction with N_2O_5 is of minor significance as a PAH loss process but (as will be discussed in the following text) may be important as a formation route of mutagenic nitro-PAH. In addition, for the PAH-containing cyclopenta-fused ring, such as acenaphthene, acenaphthylene, and acephenanthrylene, the NO_3 radical reaction can be an important gas-phase loss process during nighttime hours.

Relatively few product data are available concerning these gas-phase reactions. It has recently been shown that, in the presence of NO_x, the OH radical reactions with naphthalene, 1- and 2-methylnaphthalene, acenaphthylene, biphenyl, fluoranthene, pyrene, and acephenanthrylene lead to the formation of nitroarenes (Arey at al., 1986, 1989; Atkinson et al., 1987, 1990;

Zielinska et al., 1988, 1989a). The postulated reaction pathway involves initial OH radical addition to the most reactive ring position; for example, C-3 position for fluoranthene (Pitts et al., 1985a):
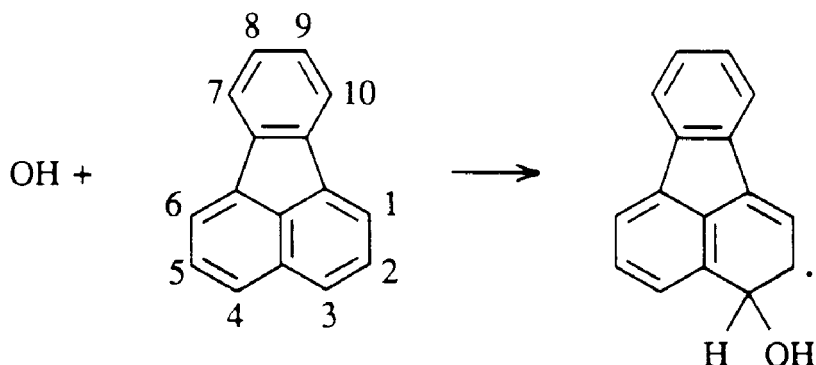
followed by NO_2 addition in the C-2 position. Subsequent elimination of water results in 2-nitrofluoranthene formation:
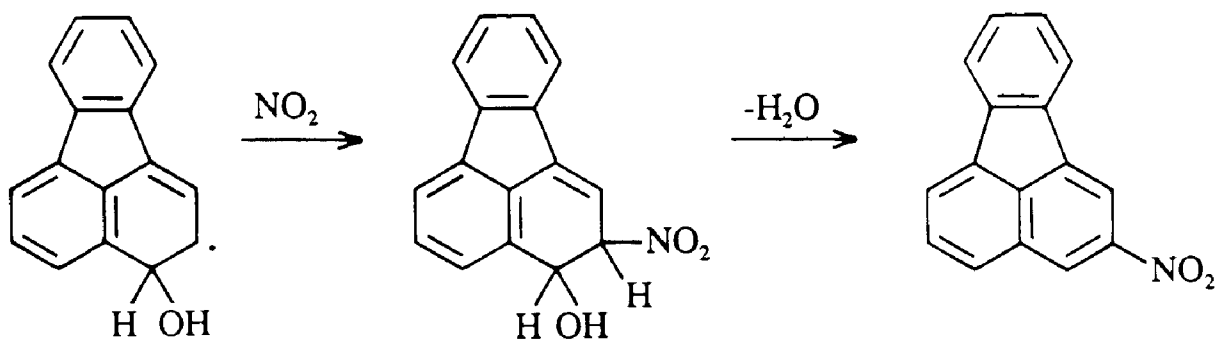
The analogous reaction sequence for pyrene produces 2-nitropyrene (2-NP) (Pitts et al., 1985a). In contrast, the electrophilic nitration reaction of fluoranthene or pyrene involving the NO_2^+ ion produces mainly 3-nitrofluoranthene (3-NF) from fluoranthene and 1-NP from pyrene.

The gas-phase reactions of N_2O_5 with naphthalene, 1- and 2-methylnaphthalene, acenaphthene, phenanthrene, anthracene, fluoranthene, and pyrene yield, in general, the same nitro-PAH isomers as the OH radical reaction but with different yields (Arey et al., 1989; Sweetman et al., 1986; Atkinson et al., 1987, 1990; Zielinska et al., 1986, 1989a). For example, the same 2-NF is produced from both OH radical and N_2O_5 gas-phase fluoranthene reactions, but the reaction with N_2O_5 produces a much higher yield. The postulated reaction pathway involves initial NO_3 radical addition to the most reactive position, followed by NO_2 addition to the neighboring position and elimination of HNO_3 (Zielinska et al., 1986):
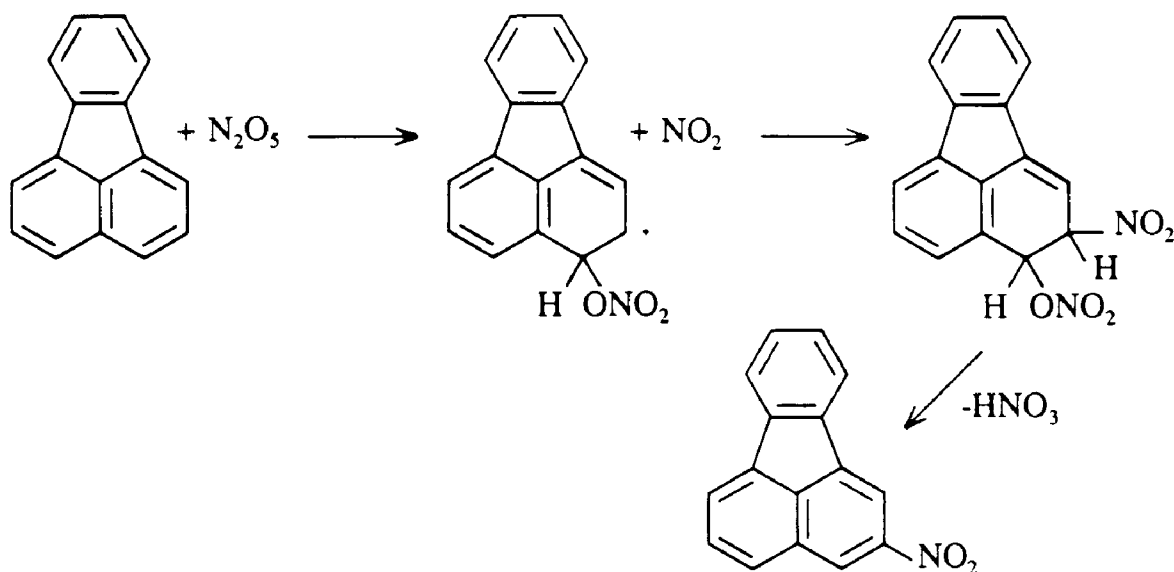
Table 2-13 summarizes the nitroarene product data for OH radical-initiated and N_2O_5 gas-phase reactions with several PAHs studied to date in environmental chambers (Arey et al., 1989; Zielinska et al., 1990). Section 2.5.3 will discuss the fact that, generally, the same nitro-PAH isomers that are formed from OH radical and N_2O_5 reactions are observed in ambient air samples.

2.4.2.2. *Particulate-Phase Reactions*

Organic compounds present in diesel exhaust are partitioned into the particulate phase under atmospheric conditions. The following chemical processes are likely to contribute to the degradation of these compounds in the troposphere (Atkinson, 1988):

- Photolysis,

- Reaction with O_3,

- Reaction with N_2O_5 during nighttime hours,

- Reaction with NO_2 during nighttime and daytime hours,

- Reaction with H_2O_2, and

- Reaction with HNO_3, HNO_2, and H_2SO_4.

However, the atmospheric lifetimes of particle-bound organic compounds are not well known, partly because (1) these chemical processes depend on the nature of the substrate (e.g., Behymer and Hites, 1985, 1988) and (2) many of the laboratory studies have been done using atmospherically unrealistic adsorbents, such as glass-fiber and Teflon-coated glass-fiber filters,

silica gel, and alumina. The extrapolation of sometimes contradictory results reported by different laboratories to atmospherically realistic conditions presents major problems.

The atmospheric fate of particle-bound PAHs has received much attention since their potential toxicity was first observed. In their recent publication, Behymer and Hites (1988) define two opposite schools of thought on this subject. One says that particle-bound PAHs degrade quickly in the atmosphere with lifetimes as short as a few hours (e.g., Kamens et al., 1988; Nielsen, 1988; Behymer and Hites, 1988). The other says that PAHs degrade slowly, if at all, in the atmosphere and eventually deposit on soil or water. The latter conclusion is supported by the studies of marine and lacustrine sediments (the ultimate environmental sinks of PAHs) that have shown that the relative abundances of PAHs, even at the most remote locations, are similar to those in combustion sources and in air particulate matter (Laflamme and Hites, 1978; Hites et al., 1980; McVeety and Hites, 1988).

2.4.2.2.1. *Photooxidation of particulate polycyclic aromatic hydrocarbons.* Laboratory studies of photolysis of PAHs adsorbed on 18 different fly ashes, carbon black, silica gel, and alumina (Behymer and Hites, 1985, 1988) and several coal stack ashes (Yokley et al., 1986; Dunstan et al., 1989) showed that the extent of photodegradation of PAHs depended very much on the nature of the substrate to which they are adsorbed. The dominant factor in the stabilization of PAHs adsorbed on fly ash was the color of the fly ash, which is related to the amount of black carbon present. It appeared that PAHs were stabilized if the black carbon content of the fly ash was greater than ≈5%. On black substrates, half-lives of PAHs studied were on the order of several days (Behymer and Hites, 1988).

Similar conclusions were reached from studies of photolysis of PAHs adsorbed on coal stack ashes (Yokley et al., 1986; Dunstan et al., 1989). The relative quantity of carbon in coal ash was the main factor determining the extent of photochemical degradation of pyrene and benzo[*a*]pyrene adsorbed on the surface. In addition, in coal ashes that contained a relatively large quantity of iron, the magnetic particles played a minor role in stabilizing adsorbed pyrene toward photodegradation (Dunstan et al., 1989).

On the other hand, the environmental chamber studies of Kamens and co-workers (1988) on the daytime decay of PAH present on residential wood smoke particles and on gasoline internal combustion emission particles showed PAH half-lives on the order of 1 h at moderate humidities and temperatures. At very low-angle sunlight, very low water-vapor concentration, or very low temperatures, PAH daytime half-lives increased to a period of days.

Atmospheric studies by Nielsen (1988), carried out in rural areas during the winter and early spring when ambient temperatures and concentrations of NO_2 and O_3 were low, showed evidence for atmospheric decay of more reactive PAHs, such as benzo[*a*]pyrene and

cyclopenteno[*cd*]pyrene. Although no estimation of these PAH lifetimes was given, the author concluded that the decay appeared to be relatively fast.

Because of the limited understanding of the mechanisms of these complex heterogeneous reactions, it is currently impossible to draw any firm conclusion concerning the photostability of particle-bound PAHs in the atmosphere. Because diesel particulate matter contains a relatively high quantity of elemental carbon (see Section 2.3.2.1), it is reasonable to assume that PAHs adsorbed onto these particles should be relatively stable under standard atmospheric conditions. Clearly, additional comprehensive and systematic investigation of adsorbed-phase reactions of PAHs is needed.

2.4.2.2.2. *Nitration of particulate polycyclic aromatic hydrocarbons under simulated atmospheres.* Since 1978, when Pitts and co-workers (Pitts et al., 1978) first demonstrated that B[*a*]P deposited on glass-fiber filters exposed to air containing 0.25 ppm of NO_2 with traces of HNO_3 formed nitro-B[*a*]P, numerous studies of the heterogeneous nitration reactions of PAHs adsorbed on a variety of substrates in different simulated atmospheres have been carried out (e.g., Finlayson-Pitts and Pitts, 1986).

PAHs deposited on glass-fiber and Teflon-impregnated glass-fiber filters react with gaseous N_2O_5, yielding their nitro derivatives (Pitts et al., 1985b,c). The nitro-PAH isomers formed from the parent PAH are the same as those formed from electrophilic nitration reactions involving NO_2^+ ions. Thus, the most abundant isomers formed were 1-NP from pyrene, 6-nitro-B[*a*]P from B[*a*]P, and 3-nitroperylene from perylene. For fluoranthene, 3-, 8-, 7-, and 1-NF isomers were formed in approximately equal amounts in N_2O_5 reactions, whereas the nitrofluoranthene isomer distribution from electrophilic nitration reaction is 3-> 8->> 7-$\geq$ 1-NF. However, no 2-NF (the sole isomer formed from gas-phase N_2O_5 reaction) was produced from this adsorbed-phase reaction (Pitts et al., 1985c). It was speculated that N_2O_5 becomes ionized on the filter surface prior to the reaction with fluoranthene, but the resulting NO_2^+ ion is not "free" nitronium ion, that is, not completely dissociated (Zielinska et al., 1986).

Based on these laboratory studies, it has been proposed that some nitro-PAHs detected in ambient particles may be formed from the reaction of the parent PAH with gaseous copollutants in the atmosphere, during the collection of particulate matter, or both (Pitts et al., 1978, 1985a; Jäger and Hanuš, 1980; Brorström et al., 1983). However, the extrapolation of the data obtained under laboratory conditions to the ambient atmosphere requires several major assumptions. These include, for example, the assumptions that substrate effect, PAH concentration, the presence of copollutants, relative humidity, etc., have no major impact on PAH nitration reactivities. If these assumptions are valid, the available data indicate that the nitration of particle-bound PAH with NO_2/HNO_3 and N_2O_5 is probably not significant under atmospheric conditions (Pitts et al.,

1985c). However, this may not always be the case in air sheds that have high NO_2 and nighttime N_2O_5 concentrations.

The formation of nitro-PAHs during sampling may be an important problem for diesel particulate matter collection because of the presence of NO_2 and HNO_3. However, Schuetzle (1983) concluded that the artifact formation of 1-NP during dilution tube sampling accounts for less than 10% to 20% of the total 1-NP present in diesel particles if the sampling time is less than 23 min (one FTP cycle) and if the sampling temperature is not higher than 43°C.

The formation of nitroarenes during ambient high-volume sampling conditions has been reported to be minimal, at least for the most abundant nitropyrene and nitrofluoranthene isomers (Arey et al., 1988).

2.4.2.2.3. *Ozonolysis of particulate polycyclic aromatic hydrocarbons.* Numerous laboratory studies have shown that PAHs deposited on combustion-generated fine particles and on model substrates undergo reaction with O_3 (e.g., Katz et al., 1979; Pitts et al., 1980, 1986; Van Vaeck and Van Cauwenberghe, 1984; Finlayson-Pitts and Pitts, 1986). The dark reaction of several PAHs deposited on model substrates toward O_3 has been shown to be relatively fast under simulated atmospheric conditions (Katz et al., 1979; Pitts et al., 1980, 1986). Half-lives of the order of one to several hours were reported for the more reactive PAHs, such as B[*a*]P, anthracene, and benz[*a*]anthracene (Katz et al., 1979).

The reaction of PAH deposited on diesel particles with 1.5 ppm O_3 under high-volume sampling conditions has been shown to be relatively fast, and half-lives of the order of 0.5 to 1 h have been reported for most PAHs studied (Van Vaeck and Van Cauwenberghe, 1984). The most reactive PAHs include B[*a*]P, perylene, benz[*a*]anthracene, cyclopenta[*cd*]pyrene, and benzo[*ghi*]perylene. The benzofluoranthene isomers are the least reactive of the PAHs studied, and benzo[*e*]pyrene (B[*e*]P) is less reactive than its isomer B[*a*]P. The implications of this study for the high-volume sampling of ambient POM are important: reaction of PAHs with O_3 could possibly occur under high-volume sampling conditions during severe photochemical smog episodes, when the ambient level of O_3 is high. However, the magnitude of this artifact is difficult to assess from available data.

Exposures of PAH adsorbed on filters and ambient particulate matter to ambient levels of O_3 in an environmental chamber under "passive" conditions, more nearly resembling atmospheric transport (as opposed to filtration-type experiments analogous to high-volume sampling of particles), also have been carried out (Pitts et al., 1986). These experiments showed that significant degradation of more reactive PAHs adsorbed on ambient particulate matter, such as B[*a*]P, pyrene, and benz[*a*]anthracene, may occur in O_3-polluted atmospheres.

2.4.3. Physical Removal Processes

2.4.3.1. *Dry Deposition*

Dry deposition is the removal of particles and gases from the atmosphere through the delivery of mass to the surface by nonprecipitation atmospheric processes and the subsequent physical attachment to, or chemical reaction with, surfaces such as vegetation, soil, water, or the built environment (Dolske and Gatz, 1985). It should be noted that the surface itself may be wet or dry; the term "dry deposition" refers to the mechanism of transport to the surface, not to the nature of the surface itself. Dry deposition plays an important role as a removal mechanism of pollutant in the absence of precipitation. Even in remote locations such as Siskiwit Lake, located on a wilderness island in northern Lake Superior, the dry deposition of aerosol was found to exceed the wet removal mechanism by an average ratio of 9:1 (McVeety and Hites, 1988).

For particles, the deposition velocities depend on the particle size, exhibiting a minimum for particles of mean diameter of ≈ 0.1 to ≈ 1 µm.

2.4.3.2. *Wet Deposition*

Wet deposition encompasses all processes by which airborne pollutants are transported to the Earth's surface in aqueous form (i.e., in rain, snow, or fog). The mechanisms of wet removal from the atmosphere may be very different for particle-associated compounds and for gas-phase compounds. However, because many organic compounds are partitioned between the aerosol and vapor phase, processes of both gas and particle scavenging may be important for a given compound (Ligocki et al., 1985a,b; Bidleman, 1988). When there is no exchange of material between the particulate and dissolved phases in the rain, the total scavenging of a given compound can be expressed as (Pankow et al., 1984):

$$W = W_g (1-\phi) + W_p \phi$$

where W is the overall scavenging ratio:

$$W = \frac{[\text{rain, total}]}{[\text{air, total}]}$$

W_g is the gas scavenging ratio:

$$W_g = \frac{[\text{rain, dissolved}]}{[\text{air, gas}]}$$

W_p is the particle scavenging ratio:

$$W_p = \frac{[\text{rain, particulate}]}{[\text{air, particulate}]}$$

and ϕ is the fraction of the atmospheric concentration that is associated with particles.

Particle scavenging is a complex process that depends on the meteorological conditions in the cloud as well as the size and chemical composition of the aerosol particles. The simplest model for in-cloud particle scavenging involves nucleation scavenging followed by coalescence or growth of the cloud droplet into raindrops.

In cold clouds, ice crystals grow by vapor accretion and by collection of supercooled droplets (riming). Scavenging ratios may be considerably lower than 10^6 under these conditions. In the case of below-cloud scavenging, W_p values have been estimated to be 10^3 to 10^5 for 0.01 to 1.0 µm particles (Slinn et al., 1978). From these data, one may expect to observe overall particle scavenging ratios in the range of 10^3 to 10^6.

Ligocki and co-workers (Ligocki et al., 1985a,b) measured gas- and particle-scavenging ratios for a number of organic compounds, including PAHs and their derivatives. Table 2-14 gives mean gas, particle, and overall scavenging ratios for measured neutral organic compounds. It can be seen from this table that particle scavenging ratios range from 10^2 to 10^5, whereas gas scavenging ratios range from 22 to 10^5. Gas scavenging dominates over particle scavenging for compounds of lower molecular weights (MW <252 for PAHs). Particle scavenging dominates for the alkanes, which are essentially insoluble in water.

The complexity of liquid-phase inorganic acid formation from gaseous precursors and the problems of acid rain and acid fog are beyond the scope of this chapter and are not discussed here (see Finlayson-Pitts and Pitts [1986] for more information).

2.5. ATMOSPHERIC CONCENTRATIONS OF PRIMARY DIESEL EMISSIONS AND THEIR TRANSFORMATION PRODUCTS

Most of the data collected on vehicle emissions are from laboratory studies that used dynamometer/dilution tube measurements. The relevance of these measurements to the atmosphere is always a question, because emissions from vehicles on the road have much higher dilution ratios ($\approx 10^3$ vs. 10), are collected at lower temperatures, are composed of a large number of individual vehicle exhausts, have usually experienced longer residence times (seconds to days versus ≈ 5 s) before collection or measurement, and, as discussed in Section 2.4, have the opportunity to interact with ambient air pollutants (including exhausts of other vehicles and vehicle types).

Pierson and co-workers (Pierson et al., 1983; Salmeen et al., 1985) conducted field experiments in the Allegheny Mountain Tunnel of the Pennsylvania Turnpike to address this problem. They found that the diesel-produced particulate matter at tunnels was, in general, very similar to that encountered in dilution-tube studies with respect to total particulate matter

Table 2-14. Mean particle, gas, and overall scavenging ratios for neutral organic compounds[a]

Compound	Mean $\emptyset$[b]	Mean W_p	Mean W_g	Mean W[c]	Dominant scav. mech.[d]
Toluene	0.0	0.0	22 ± 5	22 ± 5	g
1,2,4-Trimethylbenzene	0.0	0.0	27 ± 9	27 ± 9	g
Ethylbenzene	0.0	0.0	27 ± 1	127 ± 11	g
$m+p$-Xylene	0.0	0.0	33 ± 17	33 ± 17	g
o-Xylene	0.0	0.0	35 ± 15	35 ± 15	g
Naphthalene	0.0	0.0	250 ± 73	250 ± 73	g
2-Methylnaphthalene	0.0	0.0	250 ± 78	250 ± 78	g
1-Methylnaphthalene	0.0	0.0	330 ± 100	330 ± 100	g
Diethylphthalate	0.0	NA	20,000	20,000	g
Dibenzofuran	0.008	11,000	930	1,000	g
Fluorene	0.009	15,000	1,500	1,600	g
Phenanthrene + anthracene	0.011	17,000	3,300	3,500	g
9-Fluorenone	0.021	15,000	11,000	11,000	g
Methylphenanthrenes	0.027	13,000	2,500	2,800	g
Fluoranthene	0.053	11,000	6,300	6,600	g
Pyrene	0.071	9,300	5,900	6,100	g
Eicosane	0.14	40,000	NA	5,600	p
9,10-Anthracenedione	0.21	2,400	27,000	22,000	g
Dioctylphthalate	0.56	36,000	20,000	30,000	p
Docosane	0.61	27,000	NA	17,000	p
Chrysene	0.71	2,600	18,000	7,000	g
Benz[a]anthracene	0.75	1,300	12,000	4,000	g
Benzo[e]pyrene	0.97	2,000	5,800	2,100	p
Benzo[a]pyrene	0.98	1,700	NA	1,700	p
Benzo[$b+j+k$]fluoranthene	0.98	2,200	7,400	2,300	p
Perylene	1.0	1,800	NA	1,800	p
Tricosane	1.0	22,000	NA	22,000	p
Tetracosane	1.0	16,000	NA	16,000	p
Benzo[ghi]perylene	1.0	3,100	NA	3,100	p
Coronene	1.0	5,900	NA	5,900	p

[a]From Ligocki et al. (1985a,b).
[b]$\emptyset$ = (aerosol)/(vapor + aerosol).
[c]$W = W_p \emptyset + W_g(1-\emptyset)$.
[d]g = Gas; p = Particle.
NA = Not available.

emission rates, percentage extractables, hydrocarbon molecular weight distribution, HPLC profiles, particle size distribution, elemental compositions, and extract mutagenicities. However, these findings did not preclude the possibility of substantial differences in detailed chemical compositions. Indeed, the concentration of 1-NP in the extract of particulate samples collected in the Allegheny Mountain Tunnel was reported to be lower than would be predicted on the basis of laboratory dilution tube measurements either for diesel or spark-ignition vehicles (Gorse et al., 1983).

Some data on organic compound concentrations in air sheds heavily affected by motor vehicle emissions (tunnels, roadsides, etc.) are reviewed in the following text.

2.5.1. Volatile Organic Compounds Attributable to Traffic

Individual volatile hydrocarbons and aldehydes were measured along a section of U.S. Highway 70 near Raleigh, NC (Zweidinger et al., 1988). Traffic volume during sampling was determined by visual counting ($\approx$1,050 $\pm$ 10% vehicles per hour in each direction) and was classified into four groups: (1) light-duty, including gasoline and diesel vehicles; (2) heavy-duty gasoline; (3) HDD; and (4) motorcycles. Typical distributions were 91.5%, 3.2%, 5.1%, and 0.2%, respectively.

Table 2-15 lists the mean concentrations from four roadsides for selected hydrocarbons and aldehydes, expressed in ppb C and as a percentage contribution of individual hydrocarbons and aldehydes to total nonmethane hydrocarbons (TNMHC) and total aldehydes, respectively.

The roadside VOC distribution was compared with dynamometer/dilution tube results on in-use vehicles, which were weighted in an attempt to reflect the same model year distribution as observed on the roadway (Sigsby et al., 1987; see also Table 2-3). The two sets of data were similar in that the different driving cycles, like the different sampling sites, generally show no significant differences in the distribution of hydrocarbons or aldehydes on a percentage of total basis. There were, however, differences observed between the sets of data, particularly for the contribution of combustion products (i.e., hydrocarbons below C_4 and aldehydes). For the roadside study, ethylene, formaldehyde, and acetaldehyde were lower, whereas acetylene was higher than in the dynamometer study. However, noncatalyst vehicles, which constituted 15% of all light-duty vehicles in the roadside study, were not included in the dynamometer study, nor were LDD and HDD vehicles and trucks.

2.5.2. Polycyclic Aromatic Hydrocarbons

Particulate and vapor phase samples were collected from the traffic passing through the Baltimore Harbor Tunnel and analyzed for PAHs and related compounds (Benner et al., 1989). High-volume air samplers equipped with Teflon filters backed by PUF plugs were used for

Table 2-15. Concentrations of individual hydrocarbons and aldehydes measured in the Raleigh, NC, roadside study[a]

Compound	Concentration (ppbC)	Percent contribution[b,c]
Hydrocarbons		
Ethane	16.30	1.81
Ethylene	64.30	7.15
Acetylene	50.90	5.65
Propane	7.90	0.88
Propylene	22.60	2.51
n-Butane	15.80	1.75
1-Butene	5.70	0.64
n-Pentane	25.40	2.82
iso-Pentane	53.00	5.89
Methylcyclopentane	10.40	1.15
Methylcyclohexane	4.70	0.53
n-Decane	3.00	0.33
Benzene	29.00	3.23
Toluene	59.30	6.60
m- and *p*-Xylenes	53.10	5.90
o-Xylene	12.70	1.41
Ethylbenzene	12.00	1.33
TNMHC[d]	900.00	100.00
Total paraffins	369.20	41.00
Total olefins	164.50	18.20
Total aromatics	252.00	28.00
Total unidentified NMHC	63.60	7.10
Aldehydes		
Formaldehyde	6.74	1.05
Acetaldehyde	3.00	18.40
Acrolein	1.20	7.30
Benzaldehyde	2.31	3.88
Total aldehydes	16.38	100.00

[a]From Zweidinger et al. (1988).
[b]Percent based on ppbC.
[c]Percent contribution of individual hydrocarbons to TNMHC and of individual aldehydes to total aldehydes.
[d]TNMHC = Total nonmethane hydrocarbons.

sample collection. There was no breakdown of traffic into numbers of diesel- and gasoline-fueled vehicles.

The range of particle-phase PAH concentrations and the mean particle- and vapor-phase PAH concentrations for 48 samples collected in the tunnel are tabulated in Table 2-16. The ratios of mean particle-phase PAH concentrations to that of B[*e*]P, which is considered to be a nonreactive PAH, are also given in this table.

As can be seen from Table 2-16, alkyl-substituted phenanthrenes in the tunnel samples had relatively high concentrations compared with those of the parent compound. This suggests a significant contribution from diesel vehicle emissions (particularly diesel-fueled trucks) because extracts of diesel particulate matter are known to have significant concentrations of methyl and dimethylphenanthrenes (see Table 2-8 and Yu and Hites, 1981).

Factor analysis was applied to the tunnel data in an attempt to identify factors associated with different types of vehicles; two factors were obtained. The alkylated phenanthrenes loaded significantly on factor 1, suggesting the diesel vehicles as the source of these compounds. Several of the higher-molecular-weight PAHs loaded onto factor 2, which may be associated with the contribution of gasoline-fueled emissions in the tunnel.

Ambient air sampling for PAHs was also conducted during a summertime photochemical air pollution episode in Glendora, CA, at a site situated less than 1 km from the heavily traveled I-210 freeway and generally downwind of Los Angeles; therefore, the site was affected by motor vehicle emissions (Atkinson et al., 1988). Samples were collected by means of high-volume samplers equipped with Teflon-impregnated glass-fiber filters backed by PUF plugs. Table 2-17 shows the average (from three daytime and three nighttime samples) concentrations of PAH measured and the ratios of these concentrations to that of B[*e*]P. Unfortunately, no alkylated phenanthrenes were measured.

As can be seen from the comparison of Tables 2-16 and 2-17, the concentrations of all PAHs measured in Glendora were much lower than those measured in the tunnel, as would be expected. However, the ratios of the concentrations of particle-bound PAH to those of B[*e*]P were also different for the two sites, usually much lower for the Glendora site (except for higher molecular weight PAHs, indeno[1,2,3-*cd*]pyrene, benzo[*ghi*]perylene, and coronene). This may indicate either contributions from sources other than motor vehicles in the Glendora study or PAH photochemical transformations occurring on particles prior to or during high-volume sample collections (or both). The generally higher PAH concentrations for nighttime versus daytime sampling periods (Atkinson et al., 1988) seem to support the latter possibility. However, the influence of meteorology cannot be excluded. This conclusion is also consistent with high levels of photochemical pollutants observed in Glendora; for example, the daily maxima of O_3

Table 2-16. Particle- and vapor-phase polycyclic aromatic hydrocarbon concentrations for Baltimore Harbor Tunnel samples[a]

Compound	Range, particles	Mean, particles	Mean, vapor[b]	Ratio[c] to B[e]P
	Concentration (ng/m^3)			
Phenanthrene	4.3-56	18.0	132	4.3
Anthracene	0.6-12	2.9	18	0.6
3-Methylphenanthrene	3.9-58	13.9	70	3.3
2-Methylphenanthrene	5.3-74	19.0	—	4.6
2-Methylanthracene	0.6-12	3.0	5.3	0.7
9-and 4-Methyl-phenanthrene and 4H-cyclopenta[def]-phenanthrene	4.7-50	12.9	71	3.0
1-Methylphenanthrene	2.6-43	9.8	43	2.3
2,6-Dimethylphenanthrene	4.7-62	14.0	30	3.4
2,7-Dimethylphenanthrene	3.4-38	9.2	16	2.2
1,3-, 2,10-, 3,9-, and 3,10-Dimethyl- and phenanthrene	9.5-119	26.0	61	6.3
1,6- and 2,9-Dimethylphenanthrene	4.5-63	14.0	27	3.3
1,7-Dimethylphenanthrene	3.9-41	10.2	20	2.4
2,3-Dimethylphenanthrene	3.5-41	9.3	16	2.2
Fluoranthene	6.4-69	20.0	16	4.5
Pyrene	9.7-76	27.0	26	6.3
Benzo[ghi]fluoranthene	3.2-26	9.6	ND[d]	2.1
Cyclopenta[cd]pyrene	7.6-65	20.0	ND	4.6
Benz[a]anthracene	1.9-29	7.6	ND	1.5
Chrysene/triphenylene	2.9-47	12.0	ND	2.4
Benzofluoranthenes[b,j,+k]	2.2-44	10.6	ND	2.1
Benzo[e]pyrene	1.5-19	5.0	ND	1.0
Benzo[a]pyrene	1.3-26	5.8	ND	1.1
Indeno[1,2,3-cd]pyrene	0.3-15	4.6	ND	0.9
Benzo[ghi]perylene	1.8-18	8.0	ND	1.6
Coronene	1.0-10	4.7	ND	0.9

[a]From Benner et al. (1989).
[b]Mean concentrations of PAH collected on PUF plug (calculated from data given in Table III of Benner et al., 1989).
[c]Mean ratios to particulate phase B[e]P.
[d]None detected.

Table 2-17. Average ambient concentrations of polycyclic aromatic hydrocarbons measured in Glendora, CA[a]

PAH	Total concentration (ng/m^3)	Ratio to B[*e*]P[b]
Phenanthrene[c]	20.0	—
Anthracene[c]	1.0	—
Fluoranthene	5.6 (0.26)[d]	0.27
Pyrene	4.1 (0.35)[d]	0.37
Benzo[*ghi*]-fluoranthene	0.26	0.28
Cyclopenta[*cd*]-pyrene	0.09	0.1
Benz[*a*]anthracene	0.2	0.22
Chrysene/Triphenylene	1.0	1.1
Benzofluoranthenes[*b,j+k*]	1.6	1.7
Benzo[*e*]pyrene	0.94	1.0
Benzo[*a*]pyrene	0.33	0.35
Indeno[*1,2,3-cd*]-pyrene	1.6	1.7
Benzo[*ghi*]perylene	3.8	4.0
Coronene	2.8	3.0

[a]From Atkinson et al. (1988).
[b]Ratios of particle-phase PAH to particle-phase B[*e*]P.
[c]Phenanthrene and anthracene were not present on filters, only on PUF plugs.
[d]Fluoranthene and pyrene are distributed between gas and particulate phases; numbers in parentheses represent
 particle concentrations.

concentrations (which always occurred between 1400 and 1700 hours, Pacific standard time) ranged from 160 to 240 ppb throughout the entire 9 days of the study.

2.5.3. Nitroarene Concentrations in Ambient Air

Diesel particulate matter contains a variety of nitroarenes, with 1-NP being the most abundant among identified nitro-PAHs. The concentration of 1-NP was measured in the extract of particulate samples collected at the Allegheny Mountain Tunnel on the Pennsylvania Turnpike (Gorse et al., 1983). This concentration was 2.1 ppm and ≤5 ppm (by mass) of the extractable material from diesel and spark-ignition vehicle particulate matter, respectively. These values are much lower than would be predicted on the basis of laboratory dilution tunnel measurements for either diesel or spark-ignition engines.

Several nitroarene measurements were conducted in air sheds heavily affected by motor vehicle emissions (Arey et al., 1987; Atkinson et al., 1988; Zielinska et al., 1989a,b; Ciccioli et al., 1989). For example, ambient particulate matter samples were collected at three sites (Claremont, Torrance, and Glendora) in the Los Angeles Basin; the Claremont and Glendora sites are ≈30 km and ≈20 km northeast, respectively, and the Torrance site is ≈20 km southwest

of downtown Los Angeles (Arey et al., 1987; Atkinson et al., 1988; Zielinska et al., 1989a,b). The sampling was conducted during two summertime periods (Claremont, September 1985, and Glendora, August 1986) and one wintertime period (Torrance, January and February 1986). Table 2-18 lists the maximum concentrations of nitropyrene and nitrofluoranthene isomers observed at these three sites during the daytime and nighttime sampling periods.

As can be seen from Table 2-18, 1-NP, the most abundant nitroarene emitted from diesel engines, is not the most abundant nitroarene observed in ambient particulate matter collected at three sites heavily affected by motor vehicle emissions. Of the two nitropyrene isomers present, 2-NP, the main nitropyrene isomer formed from the gas-phase OH radical-initiated reaction with pyrene (see Section 2.4.2.1), is sometimes more abundant. The 2-NF was always the most abundant nitroarene observed in ambient particulate matter collected at these three sites (Ciccioli et al., 1989), and this nitrofluoranthene isomer is not present in diesel and gasoline vehicle emissions. The 2-NF is the only nitroarene produced from the gas-phase OH radical-initiated

Table 2-18. Maximum concentrations of nitrofluoranthene (NF) and nitropyrene (NP) isomers observed at three South Coast Air Basin sampling sites

Nitroarene, collection period	Concentration (pg/m^3) at		
	Claremont[a,b]	Glendora[c,d]	Torrance[a,e]
2-NF, day	40	350	410
2-NF, night	1,700	2,000	750
3-NF, day	3	ND[f]	≈3
3-NF, night	≈3	ND	70
8-NF, day	2	3	8
8-NF, night	2	4	50
1-NP, day	3	15	60
1-NP, night	10	15	50
2-NP, day	1	14	50
2-NP, night	8	32	60

[a]From Zielinska et al. (1989b).
[b]Daytime sample collected from 1200 to 1800 hours and nighttime sample from 1800 to 2400 hours on September 13, 1985.
[c]From Atkinson et al. (1988).
[d]Daytime sample collected from 0800 to 2000 hours on August 20, 1986, and nighttime sample from 2000 to 0800 hours on August 20 and 21, 1986.
[e]Daytime sample collected from 0500 to 1700 hours on January 28, 1986, and nighttime sample from 1700 to 0500 hours on January 27 and 28, 1986.
[f]ND = None detected.

N_2O_5 reactions with fluoranthene (see Sections 2.4.2.1 and 2.4.2.2), whereas mainly 3-NF and lesser amounts of 1-, 7-, and 8-nitroisomers are present in diesel particulate matter and are produced from the electrophilic nitration reactions of fluoranthene. Figure 2-4 compares the nitroarenes formed from the OH radical-initiated reaction of fluoranthene and pyrene in an environmental chamber (upper trace) with the ambient samples collected at Torrance (lower trace). It is very unlikely that N_2O_5 could have been present during the nighttime winter collections in Torrance, given the high level of NO present at sunset. More likely, a relatively high level of OH radicals was present because of the measured high concentration of HNO_2, which photolyzes to yield OH radicals. This suggests that all isomers observed in Figure 2-4 (lower trace), with the exception of 1-NP, are the product of the OH radical-initiated reactions of the parent PAH. Direct emissions may account for the 1-NP (and 3-NF) observed at relatively low levels in these ambient samples. (See Zielinska et al. [1989b] for full discussion of all the MW 247 nitroarenes observed in ambient particles.)

Although the reaction with OH radicals is the major atmospheric loss process for gas-phase fluoranthene and pyrene (Table 2-12), evidence for atmospheric formation of 2-NF from N_2O_5 reaction with fluoranthene has also been reported (Zielinska et al., 1989b). Because the 2-NF/2-NP yield ratio for N_2O_5 reactions, observed from environmental chamber experiments, is >100, compared to ≈10 for the OH radical reaction (Table 2-4), the high 2-NF/2-NP concentration ratio in ambient samples suggests a contribution from the N_2O_5 reaction with fluoranthene. Figure 2-5 shows a comparison of a wintertime sample collected in Torrance (upper trace) with a summertime sample collected in Claremont (lower trace). The 2-NF/2-NP ratio reached ≈200 for the summer night sample. The N_2O_5 concentration was calculated to be 5 ppb for this night, which supports the suggested formation route of 2-NF via reaction with N_2O_5 (Zielinska et al., 1989b).

The evidence presented in the preceding text, as well as the observation that 2-NF has been the most abundant MW 247 nitroarene in ambient samples collected worldwide (Ramdahl et al., 1986), strongly suggests that the atmospheric formation from the parent PAH, not the direct automotive emissions, is the major source of these nitroarenes in ambient air. However, under certain sampling conditions, when ambient particulate matter is collected very close to emission sources, the MW 247 nitroarene profile may be different. For example, in urban samples collected during wintertime rush hours at a central square in Rome, Italy, at a height of 1.5 m above street level, 2-NF and 2-NP were not observed (Ciccioli et al., 1989).
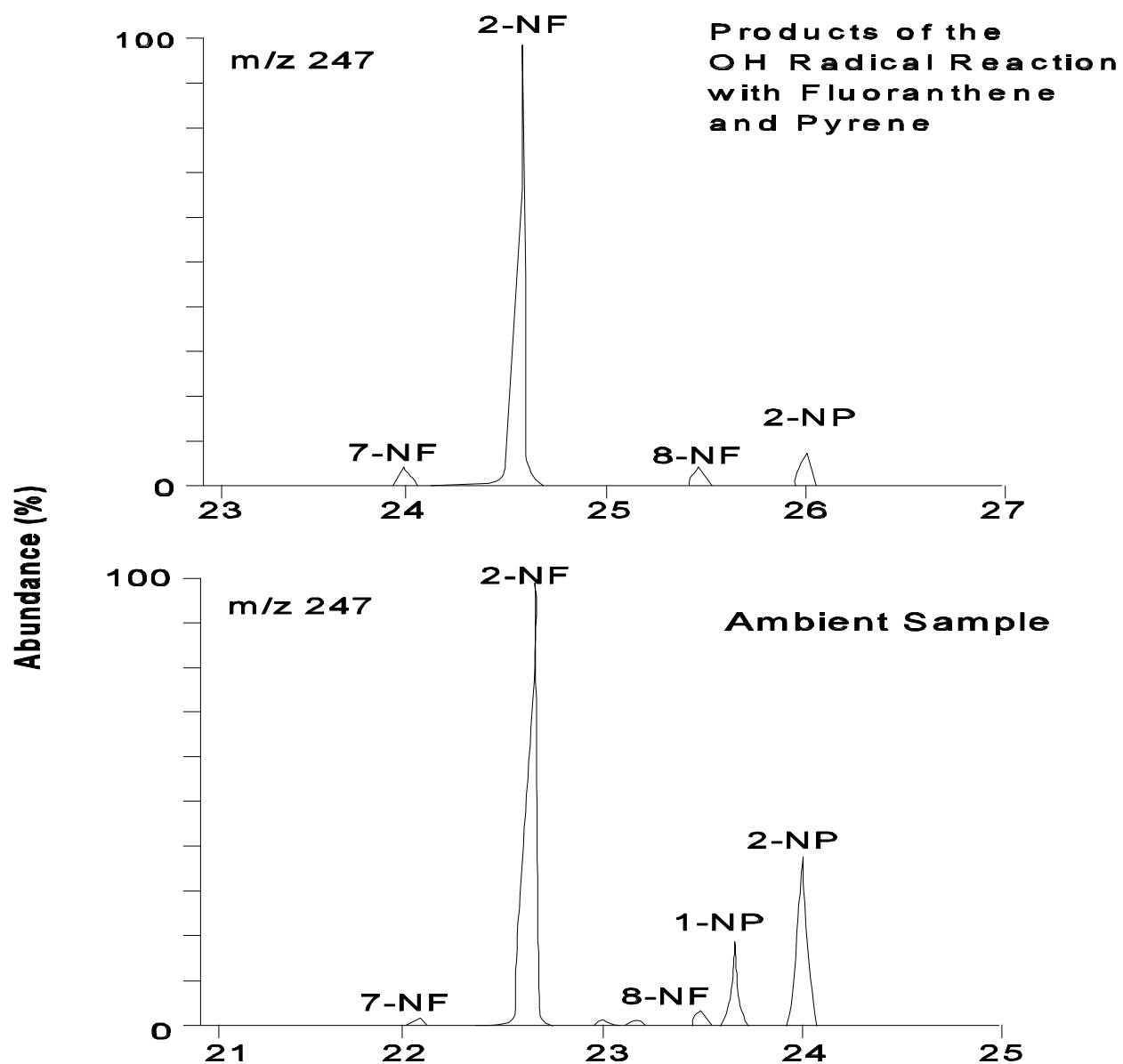
Figure 2-4. Mass chromatograms of the molecular ion of the nitrofluoranthenes (NF) and nitropyrenes (NP) formed from the gas-phase reaction of fluoranthene and pyrene with the OH radicals (top) and present in the ambient particulate sample collected at Torrance, CA (bottom).
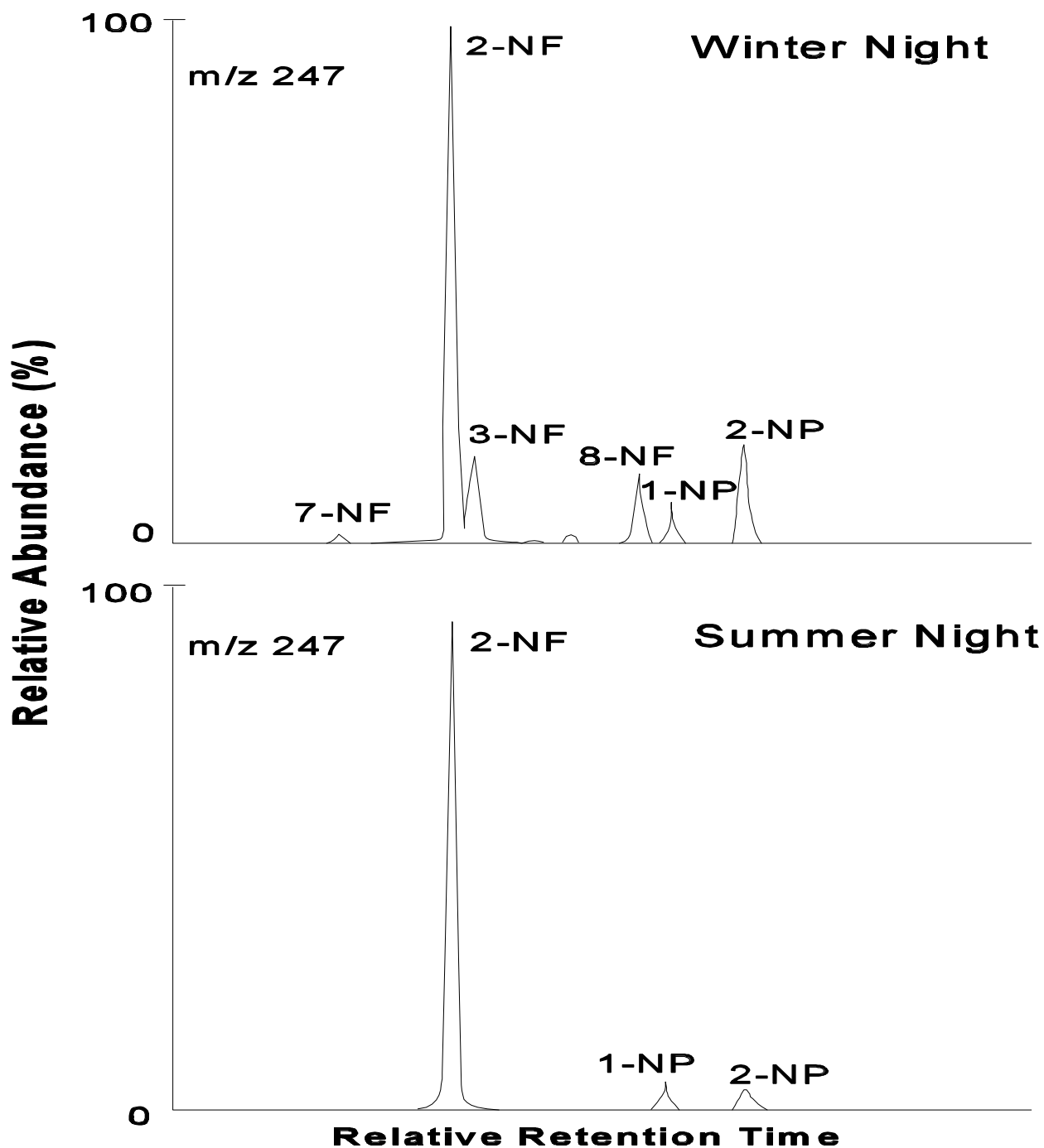
Source: Arey et al. (1989).

Figure 2-5. Mass chromatograms of the molecular ion of the nitrofluoranthenes (NF) and nitropyrenes (NP) present in ambient particulate samples collected in Torrance, CA (top), and Claremont, CA (bottom).

2.6. EXPOSURE PERSPECTIVE

Diesel emissions are complex mixtures containing thousands of organic and inorganic constituents in both gas and particulate phases and with differing chemical reactivities. After entering the atmosphere, they are transported and transformed according to their distinctive characteristics, undergoing physical and chemical changes that may form secondary pollutants more harmful than their predecessors. Thus, a knowledge of diesel emissions at or near their sources is not sufficient to fully assess the impact of these emissions on human health and welfare. However, data on how diesel exhaust contributes to exposure levels for these secondary pollutants are currently lacking.

Determining the amount of diesel exhaust present in the ambient air is also complicated by the difficulty of distinguishing organic compounds and particles that originate in diesel engines from those that originate in gasoline engines or come from other sources. This, too, cannot be accomplished at present because of the lack of a sufficient research base.

Nonoccupational exposure to diesel exhaust is worldwide in urban areas, with lesser exposure in rural areas. Certain working populations are also exposed to higher levels of diesel exhaust than the rest of the population. The level of exposure will differ within geographic areas based on the number and types of diesel engines in the area, as well as atmospheric patterns of dispersal and the location of the individual relative to the emission sources.

While a detailed exposure assessment for DE has not been conducted as part of this study, the following exposure data are provided to give some context for the hazard assessment and dose-response analysis.

Estimates of annual average concentrations of particulate matter in the ambient air, published in Chapter 9 of EPA's Motor Vehicle-Related Air Toxics Study (U.S. EPA, 1993), may be used to generate a crude estimate of the concentration of particulates from diesel exhaust in the ambient air. The Air Toxics study used two approaches to generate exposure estimates. In the first one, DPM (diesel particulate matter) national fleet average emissions factors for 1988 were multiplied by the urban and rural grams-per-meter conversion factors obtained from EPA's hazardous air pollution exposure model (HAP-EM: 1988). Based on this approach, the total concentration of particulates from diesel exhaust in ambient air in urban areas for 1995 was estimated as 2 $\mu g/m^3$; the concentration in rural areas as 0.6 $\mu g/m^3$; and the nationwide average concentration as 1.1 $\mu g/m^3$.

In a second method, using ambient monitoring data, total suspended particulate matter (TSP) for 1990 was determined to equal 48 $\mu g/m^3$. Approximately 5% of total particulate matter is associated with diesel exhaust. Multiplication of the total by the fraction contributed by diesel exhaust, and adjusting for time spent indoors, results in an integrated estimate of 1.5 $\mu g/m^3$ (U.S. EPA, 1993).

Exposure estimates for more highly polluted locations are somewhat greater. Estimated mean concentrations of DPM for Los Angeles were reported to be 2.7 µg/m^3 (Sienicki and Mago, 1992). McClellan at al. (1986) estimated concentrations on urban freeways and street canyons to be as great as 15 µg/m^3. These exposure estimates are summarized in Table 2-19.

Recent Cal-EPA (1996) studies show winter period estimates in three California locations for diesel PM$_{10}$ of 4 to 22 µg/m^3. A broader Cal-EPA analysis shows average ambient outdoor diesel PM$_{10}$ to range from 0.2 to 3.6 µg/m^3 across 14 California air basins with a population-weighted average of 3.2 µg/m^3. Concentrations in occupational settings may be higher.

Potentially, diesel exhaust may contribute to levels of a very hazardous pollutant, dioxin. Only scant information is available to quantify this, though some study data are available. Dioxin concentrations were measured in a Baltimore tunnel used only by heavy trucks (unpublished). Measurements were also made of the exhaust from a heavy-duty truck during highway travel. Based on these measurements, estimated dioxin production from all truck diesels was estimated to be only 29 gm versus 5,000 gm from all combustion sources in the United States. It is therefore concluded that DE contribution to dioxin levels in the United States is insignificant.

The changing composition of DE, (i.e., older engines vs. newer technology ones, heavy-duty vs. light-duty, and engines run under varied operating conditions) gives rise to questions about how the health data and the risk assessment findings in this report, which are based on pre-1998 engines, can be applied to present-day engine exhaust emissions and the resulting ambient

Table 2-19. Estimated annual ambient concentrations of diesel exhaust particulate matter (µg/m^3)

Year	U.S. EPA (1993) Method 1 Rural	U.S. EPA (1993) Method 1 Urban	U.S. EPA (1993) Method 1 National	U.S. EPA (1993) Method 2 National	Sienicki and Mago (1992) Los Angeles	McClellan (1986) Highly Exposed
1986						15.0
1990	1.1	2.0	1.8	1.5	2.7	
1995	0.6	1.2	1.1			
2000	0.4	0.7	0.6			
2010	0.2	0.4	0.4			

exposures. This is a complex question that is not rigorously addressed in this version of the assessment. It is clear that newer technology engines will have somewhat different emission composition (i.e., perhaps reduced NO_x with increased fine particles), not to mention the emission controls, which would reduce certain exhaust components, presumably larger particles. Since particle mass is the surrogate dosimeter used to correlate toxicity with exposure and public health impact, as the particle mass is changed by virtue of new technology or controls, so might the applicability of the health assessment findings in this report. Further analysis of emission changes may be a desirable research pursuit.

2.7. SUMMARY

Major research programs were carried out in the late 1970s and early 1980s to ascertain the physical and chemical characteristics of emissions from diesel engines and the biological effects of these emissions. New control technologies are being introduced into currently manufactured diesel vehicles, and the effect of these changes on diesel emissions is likely to be visible in the future. Diesel vehicles manufactured in the late 1970s and early 1980s are still on the road and, in this sense, data collected from that period are still valid.

However, many of these data were collected using laboratory dynamometers with selected new vehicles or vehicles well tuned to manufacturers' specifications. The well-controlled conditions of the dynamometer tests have many benefits but do not necessarily represent vehicle emissions under real on-road conditions, and the small number of vehicles tested in the laboratory is not truly representative of the distribution within the on-road vehicle fleet. Although several roadway and tunnel emission measurements were performed in the past, the database on mobile-source emission rates necessary to assess the role of vehicle emissions in air pollution problems is still not sufficient. More measurements carried out under realistic on-road conditions are necessary, in particular for gaseous and particulate-phase organic compounds present in vehicle emissions.

Once released into the atmosphere, diesel emissions are subject to dispersion and transport and, at the same time, to chemical and physical transformation into secondary pollutants, which may be more harmful than their precursors. Thus, a knowledge of diesel emissions at or near their sources is no longer sufficient to assess fully the impact of these emissions on human health and welfare. The understanding of physical and chemical changes that primary diesel emissions undergo during their transport through the atmosphere is equally important. As a result of the past two decades of laboratory and ambient experiments and computer modeling, a comprehensive set of data now exists concerning the atmospheric loss processes and transformation of automotive emissions, but knowledge concerning the products of these chemical transformations is still limited. Study is required to determine the products from the OH

radical-initiated reactions of the aromatic and aliphatic hydrocarbons from automobile emissions. The atmospheric transformation products of PAHs and their oxygen-, sulfur-, and nitrogen-containing analogs require study in the gaseous and adsorbed phases. In particular, the reactions occurring in adsorbed phases on atmospherically relevant surfaces are poorly understood and require further study. In addition, gas-to-particle conversion processes and the chemical processes that lead to aerosol formation should be further investigated.

The quantitation of the contribution of diesel emissions to total ambient aerosol mass concentration is not possible without developing a specific profile for diesel emissions, a "fingerprint" that may be used in receptor source apportionment models. The data indicate that it may be possible to use PAHs and/or alkylated PAHs, alkanes, and possibly certain unique compounds to assist in distinguishing between diesel and other pollutant sources. However, the available data are not adequate for use in receptor modeling, and study is required to determine the profile of diesel emissions by using sampling and analytical methods appropriate to receptor modeling.

2.8. REFERENCES

Alkidas, AC. (1988) Effects of injector-tip configuration on the performance and emissions of an uncooled diesel. Presented at: International fuels and lubricants meeting and exposition; October; Portland, OR. Warrendale, PA: Society of Automotive Engineers, Inc.; SAE technical paper no. 881613.

Alsberg, T; Stenberg, U; Westerholm, R; Strandell, M; Rannug, U; Sundvall, A; Romert, L; Bernson, V; Pettersson, B; Toftgärd, R; Franzén, B; Jansson, M; Gustafsson, JÅ; Egebäck, KE; Tejle, G. (1985) Chemical and biological characterization of organic material from gasoline exhaust particles. Environ Sci Technol 19:43-50.

Arey, J; Zielinska, B; Atkinson, R; Winer, AM; Ramdahl, T; Pitts, JN, Jr. (1986) The formation of nitro-PAH from the gas-phase reactions of fluoranthene and pyrene with the OH radical in the presence of NO$_x$. Atmos Environ 20:2339-2345.

Arey, J; Zielinska, B; Atkinson, R; Winer, AM. (1987) Polycyclic aromatic hydrocarbon and nitroarene concentrations in ambient air during a wintertime high-NO$_x$ episode in the Los Angeles basin. Atmos Environ 21:1437-1444.

Arey, J; Zielinska, B; Atkinson, R; Winer, AM. (1988) Formation of nitroarenes during ambient high-volume sampling. Environ Sci Technol 22:457-462.

Arey, J; Zielinska, B; Atkinson, R; Aschmann, SM. (1989) Nitroarene products from the gas-phase reactions of volatile polycyclic aromatic hydrocarbons with OH radical and N$_2$O$_5$. Int J Chem Kinet 21:775-799.

Atkinson, R. (1988) Atmospheric transformations of automotive emissions. In: Watson, AY; Bates, RR; Kennedy, D, eds. Air pollution, the automobile, and public health. Washington, DC: National Academy Press; pp. 99-132.

Atkinson, R. (1990) Gas-phase tropospheric chemistry of organic compounds: a review. Atmos Environ Part A 24:1-41.

Atkinson, R; Carter, WPL. (1984) Kinetics and mechanisms of the gas-phase reactions of ozone with organic compounds under atmospheric conditions. Chem Rev 84:437-470.

Atkinson, R; Arey, J; Zielinska, B; Aschmann, SM. (1987) Kinetics and products of the gas-phase reactions of OH radicals and N_2O_5 with naphthalene and biphenyl. Environ Sci Technol 21:1014-1022.

Atkinson, R; Arey, J; Winer, AM; Zielinska, B. (1988) A survey of ambient concentrations of selected polycyclic aromatic hydrocarbons (PAH) at various locations in California [final report]. Sacramento, CA: California Air Resources Board; contract no. A5-185-32.

Atkinson, R; Arey, J; Zielinska, B; Aschmann, SM. (1990) Kinetics and nitro-products of the gas-phase OH and NO_3 radical-initiated reactions of naphthalene-d_8, fluoranthene-d_{10} and pyrene. Int J Chem Kinet 22:999-1014.

Bailey, JC; Schmidl, B; Williams, ML. (1990) Speciated hydrocarbon emissions from vehicles operated over the normal speed range on the road. Atmos Environ Part A 24:43-52.

Ball, DJ. (1987) Particulate carbon emissions and diesel vehicles. In: Vehicle emissions and their impact on European air quality: proceedings of the Institution of Mechanical Engineers international conference; November; London, United Kingdom. London, Mechanical Engineering Publications Limited, pp. 83-88.

Balzotti, A; Cornetti, GM; Pidello, F; Signer, M; Scorsone, V. (1990) Italian city buses with particulates traps. Presented at: International congress and exposition; February-March; Detroit, MI. Warrendale, PA: Society of Automotive Engineers, Inc.; SAE technical paper no. 900114.

Bayona, JM; Markides, KE; Lee, ML. (1988) Characterization of polar polycyclic aromatic compounds in a heavy-duty diesel exhaust particulate by capillary column gas chromatography and high-resolution mass spectrometry. Environ Sci Technol 22:1440-1447.

Beck, NJ; Uyehara, OA. (1987) Factors that affect BSFC and emissions for diesel engines: Part II. Experimental confirmation of concepts presented in part I. Presented at: SAE International Congress and Exposition; February; Detroit, MI. Warrendale, PA: Society of Automotive Engineers, Inc.

Behymer, TD; Hites, RA. (1985) Photolysis of polycyclic aromatic hydrocarbons adsorbed on simulated atmospheric particulates. Environ Sci Technol 19:1004-1006.

Behymer, TD; Hites, RA. (1988) Photolysis of polycyclic aromatic hydrocarbons adsorbed on fly ash. Environ Sci Technol 22:1311-1319.

Benner, BA, Jr; Gordon, GE; Wise, SA. (1989) Mobile sources of atmospheric polycyclic aromatic hydrocarbons: a roadway tunnel study. Environ Sci Technol 23:1269-1278.

Bidleman, TF. (1988) Atmospheric processes. Environ Sci Technol 22:361-367.

Bjørseth, A; Olufsen, BS. (1983) Long-range transport of polycyclic aromatic hydrocarbons. In: Bjørseth, A, ed. Handbook of polycyclic aromatic hydrocarbons. New York: Marcel Dekker, Inc.; pp. 507-524.

Black, F; High, L. (1979) Methodology for determining particulate and gaseous diesel hydrocarbon emissions. Warrendale, PA: Society of Automotive Engineers, Inc.; SAE technical paper no. 790442.

Black, F; Braddock, J; Bradow, RL; Ingalls, M. (1985) Highway motor vehicles as sources of atmospheric particles. Environ Int 11:1-32.

Boone, PM; Macias, ES. (1987) Methyl alkanes in atmospheric aerosols. Environ Sci Technol 21:903-909.

Bradow, RL. (1980) Diesel particle emissions. Bull NY Acad Med 56:797-811.

Bradow, RL. (1982) Diesel particle and organic emissions: engine simulation, sampling, and artifacts. In: Lewtas, J., ed. Toxicological effects of emissions from diesel engines: proceedings of the Environmental Protection Agency 1981 diesel

emissions symposium; October 1981; Raleigh, NC. (Developments in toxicology and environmental science: v. 10). New York: Elsevier Biomedical,pp. 33-47.

Brorström, E; Grennfelt, P; Lindskog, A. (1983) The effect of nitrogen dioxide and ozone on the decomposition of particle-associated polycyclic aromatic hydrocarbons during sampling from the atmosphere. Atmos Environ 17:601-605.

Broukhiyan, EMH; Lestz, SS. (1981) Ethanol fumigation of a light duty diesel engine. In: SP-503 alternate fuels for diesel engines. Warrendale, PA: Society of Automotive Engineers, pp. 15-25; SAE technical paper no. 811209.

California Environmental Protection Agency (Cal-EPA). (1996) Health risk assessment for diesel exhaust, public and scientific panel review draft; Office of Environmental Health Hazard Assessment, California Environmental Protection Agency.

Campbell, RM; Lee, ML. (1984) Capillary column gas chromatographic determination of nitro polycyclic aromatic compounds in particulate extracts. Anal Chem 56:1026-1030.

Carey, P; Cohen, J. (1980) Comparison of gas phase hydrocarbon emissions from light-duty vehicles equipped with diesel engines. U.S. Environmental Protection Agency technical report no. CTAB/PA/80-5.

Cass, GR. (1990) Risk assessment of diesel exhaust: 1990 and beyond. Presented at a workshop, March, Los Angeles, CA. Sacramento, CA: California Air Resources Board.

Cass, GR; McRae, GJ. (1983) Source-receptor reconciliation of routine air monitoring data for trace metals: an emission inventory assisted approach. Environ Sci Technol 17:129-139.

Cautreels, W; Van Cauwenberghe, K. (1978) Experiments on the distribution of organic pollutants between airborne particulate matter and the corresponding gas phase. Atmos Environ 12:1133-1141.

Ciccioli, AP; Cecinato, A; Brancaleoni, E; Draisci, R; Liberti, A. (1989) Evaluation of nitrated polycyclic aromatic hydrocarbons in anthropogenic emission and air samples: a possible means of detecting reactions of carbonaceous particles in the atmosphere. Aerosol Sci Technol 10:296-310.

Clark, DH; Johnson, DM; Swedberg, SE. (1984) Modern engine oils. Warrendale, PA: Society of Automotive Engineers, Inc.; SAE technical paper no. 841207; SAE SP-603.

Coutant, RW; Brown, L; Chuang, JC; Riggin, RM; Lewis, RG. (1988) Phase distribution and artifact formation in ambient air sampling for polynuclear aromatic hydrocarbons. Atmos Environ 22:403-409.

Daisey, JM; Cheney, JL; Lioy, PJ. (1986) Profiles of organic particulate emissions from air pollution sources: status and needs for receptor source apportionment modeling. J Air Pollut Control Assoc 36:17-33.

Dietzmann, HE; Parness, MA; Bradow, RL. (1980) Emissions from trucks by chassis version of 1983 transient procedure. Presented at: Society of Automotive Engineers fuels and lubricants meeting; October; Baltimore, MD. Warrendale, PA: Society of Automotive Engineers, Inc., paper no. 801371.

Dietzmann, HE; Parness, MA; Bradow, RL. (1981) Emissions from gasoline and diesel delivery trucks by chassis transient cycle. Presented at: ASME energy-sources technology conference and exhibition; January; Houston, TX. New York: American Society of Mechanical Engineers, ASME paper no. 81-DGP-6.

Dolske, DA; Gatz, DF. (1985) A field intercomparison of methods for the measurement of particle and gas dry deposition. J Geophys Res 90:2076-2084.

Dunstan, TDJ; Mauldin, RF; Jinxian, Z; Hipps, AD; Wehry, EL; Mamantov, G. (1989) Adsorption and photodegradation of pyrene on magnetic, carbonaceous, and mineral subfractions of coal stack ash. Environ Sci Technol 23:303-308.

Dutcher, JS; Sun, JD; Lopez, JA; Wolf, I; Wolff, RK; McClellan, RO. (1984) Generation and characterization of radiolabeled diesel exhaust. Am Ind Hyg Assoc J 45:491-498.

Fenimore, CP; Jones, GW. (1967) Oxidation of soot by hydroxyl radicals. J Phys Chem 71:593-597.

Finlayson-Pitts, BJ; Pitts, JN, Jr. (1986) Atmospheric chemistry: fundamentals and experimental techniques. New York: John Wiley & Sons.

Frey, JW; Corn, M. (1967) Diesel exhaust particulates. Nature (London) 216:615-616.

Galloway, JN; Whelpdale, DM. (1980) An atmospheric sulfur budget for eastern North America. Atmos Environ 14:409-417.

Garrigues, P; Parlanti, E; Radke, M; Bellocq, J; Willsch, H; Ewald, M. (1987) Identification of alkylphenanthrenes in shale oil and coal by liquid and capillary gas chromatography and high-resolution spectrofluorimetry (Shpol'skii effect). J Chromatogr 395:217-228.

Gibbs, RE; Hyde, JD; Byer, SM. (1980) Characterization of particulate emissions from in-use diesel vehicles. Presented at: Fuels and lubricants; October; Baltimore, MD. Warrendale, PA: Society of Automotive Engineers, Inc., SAE technical paper no. 801372.

Gibson, TL. (1983) Sources of direct-acting nitroarene mutagens in airborne particulate matter. Mutat Res 122:115-121.

Gibson, TL; Ricci, AI; Williams, RL. (1981) Measurement of polynuclear aromat Society of Automotive Engineers, Inc., SAE technical paper no. 880350.

Gorse, RA, Jr.; Salmeen, IT; Clark, CR. (1982) Effects of filter loading and filter type on the mutagenicity and composition of diesel exhaust particulate extracts. Atmos Environ 16:1523-1528.

Gorse, RA, Jr; Riley, TL; Ferris, FC; Pero, AM; Skewes, LM. (1983) 1-Nitropyrene concentration and bacterial mutagenicity in on-road vehicle particulate emissions. Environ Sci Technol 17:198-202.

Gray, HA. (1986) Control of atmospheric fine primary carbon particle concentration [PhD thesis]. Pasadena, CA: California Institute of Technology; EQL report no. 23.

Hammerle, RH; Schuetzle, D; Adams, W. (1994) A perspective on the potential development of environmentally acceptable light-duty diesel engines. Environ Health Perspect (Suppl) 102(4):25-30.

Hampton, CV; Pierson, WR; Harvey, TM; Updegrove, WS; Marano, RS. (1982) Hydrocarbon gases emitted from vehicles on the road. 1. A qualitative gas chromatography/mass spectrometry survey. Environ Sci Technol 16:287-298.

Hampton, CV; Pierson, WR; Schuetzle, D; Harvey, TM. (1983) Hydrocarbon gases emitted from vehicles on the road. 2. Determination of emission rates from diesel and spark-ignition vehicles. Environ Sci Technol 17:699-708.

Hardenberg, HO; Daudel, HL; Erdmannsdorfer, HJ. (1987) Experiences in the development of ceramic fiber coil particulate traps. In: Diesel particulates: an update, SP-702. Warrendale, PA: Society of Automotive Engineers, SAE technical paper no. 870015.

Hare, CT; Bradow, RL. (1979) Characterization of heavy-duty gaseous and particulate emissions and effects of fuel composition. Warrendale, PA: Society of Automotive Engineers, Inc., SAE technical paper no. 790490.

Hare, CT; Baines, TM. (1979) Characterization of particulate and gaseous emissions from two diesel automobiles as functions of fuel and driving cycle. Presented at: Automotive engineering congress and exposition; February-March; Detroit, MI. Warrendale, PA: Society of Automotive Engineers; SAE technical paper no. 790424.

Hare, CT; Springer, KJ; Bradow, RL. (1976) Fuel and additive effects on diesel particulate development and demonstration of methodology. Presented at: Automotive engineering congress and exposition; February; Detroit, MI. Warrendale, PA: Society of Automotive Engineers, Inc., SAE technical paper no. 760130.

Harris, GW; Mackay, GI; Iguchi, T; Schiff, HI; Schuetzle, D. (1987) Measurement of NO_2 and HNO_3 in diesel exhaust gas by tunable diode laser absorption spectrometry. Environ Sci Technol 21:299-304.

Health Effects Institute. (1995) Diesel exhaust: a critical analysis of emissions, exposure, and health effects. Cambridge, MA: Health Effects Institute.

Henein, NA; Bolt, JA. (1967) Ignition lag in diesel engines. Warrendale, PA: Society of Automotive Engineers, Inc., SAE technical paper no. 670007.

Herr, JD; Yergey, JA; Dukovich, M; Tejada, S; Risby, TH; Lestz, SS. (1983) The role of nitrogen in the observed microbial mutagenic activity for diesel engine combustion. Warrendale, PA: Society for Automotive Engineers, SAE technical paper no. 820467.

Hites, RA; Laflamme, RE; Windsor, JG, Jr. (1980) Polycyclic aromatic hydrocarbons in marine/aquatic sediments: their ubiquity. In: Petrakis, L; Weiss, FT, eds. Petroleum in the marine environment [proceedings of a symposium at the 176th meeting of the American Chemical Society; September 1978; Miami Beach, FL]. (Comstock, MJ, ed. Advances in chemistry series: v. 185). Washington, DC: American Chemical Society; pp. 289-311.

Horvath, H; Kreiner, I; Norek, C; Preining, O; Georgi, B. (1988) Diesel emissions in Vienna. Atmos Environ 22:1255-1269.

Huisingh, J; Bradow, R; Jungers, R; Claxton, L; Zweidinger, R; Tejada, S; Bumgarner, J; Duffield, F; Waters, M; Simmon, VF; Hare, C; Rodriguez, C; Snow, L. (1978) Application of bioassay to the characterization of diesel particle emissions. In: Waters, MD; Nesnow, S; Huisingh, JL; Sandhu, SS; Claxton, L, eds. Application of short-term bioassays in the fractionation and analysis of complex environmental mixtures: proceedings of a symposium; February; Williamsburg, VA. (Hollaender, A; Probstein, F; Welch, BL, eds. Environmental science research: v. 15). New York: Plenum Press, pp. 383-418.

International Agency for Research on Cancer. (1989) Diesel and gasoline engine exhausts and some nitroarenes. (IARC monographs on the evaluation of carcinogenic risks to humans: v. 46). Lyon, France: World Health Organization.

Jäger, J; Hanuš, V. (1980) Reaction of solid carrier-adsorbed polycyclic aromatic hydrocarbons with gaseous low-concentrated nitrogen dioxide. J Hyg Epidemiol Microbiol Immunol 24:1-15.

Japar, SM; Szkarlat, AC; Gorse, RA, Jr; Heyerdahl, EK; Johnson, RL; Rau, JA; Huntzicker, JJ. (1984) Comparison of solvent extraction and thermal-optical carbon analysis methods: application to diesel vehicle exhaust aerosol. Environ Sci Technol 18:231-234.

Jensen, TE; Hites, RA. (1983) Aromatic diesel emissions as a function of engine conditions. Anal Chem 55:594-599.

Kadota, T; Henein, NA. (1981) Time-resolved soot particulates in diesel spray combustion. In: Siegla, DC; Smith, GW, eds. Particulate carbon: formation during combustion [proceedings of an international symposium; October 1981; Warren, MI]. New York: Plenum Press, pp. 391-421.

Kagami, M; Akasaka, Y; Date, K; Maeda, T. (1984) The influence of fuel properties on the performance of Japanese automotive diesels. Warrendale, PA: Society of Automotive Engineers, Inc.; SAE technical paper no. 841082, SAE SP-581.

Kahn, IM. (1970) Formation and combustion of carbon in a diesel engine. In: Diesel engine combustion symposium; April. London: Institute of Mechanical Engineers.

Kamens, RM; Guo, Z; Fulcher, JN; Bell, DA. (1988) Influence of humidity, sunlight, and temperature on the daytime decay of polyaromatic hydrocarbons on atmospheric soot particles. Environ Sci Technol 22:103-108.

Katz, M; Chan, C; Tosine, H; Sakuma, T. (1979) Relative rates of photochemical and biological oxidation (*in vitro*) of polycyclic aromatic hydrocarbons. In: Jones, PW; Leber, P, eds. Polynuclear aromatic hydrocarbons: third international symposium on chemistry and biology—carcinogenesis and mutagenesis; October 1978; Columbus, OH. Ann Arbor, MI: Ann Arbor Science Publishers, Inc.; pp. 171-189.

Kawamura, K; Ng, L-L; Kaplan, IR. (1985) Determination of organic acids (C_1-C_{10}) in the atmosphere, motor exhausts and engine oil. Environ Sci Technol 19:1092-1096.

Kittelson, DB; Dolan, DF. (1980) Diesel exhaust aerosols. In: Willeke, K, ed. Generation of aerosols and facilities for exposure experiments: [technical papers presented at the symposium on aerosol generation and exposure facilities]; April 1979; Honolulu, HI. Ann Arbor, MI: Ann Arbor Science; pp. 337-359.

Kleindienst, TE; Shepson, PB; Edney, EO; Claxton, LD. (1985) Peroxyacetyl nitrate: measurement of its mutagenic activity using the Salmonella/mammalian microsome reversion assay. Mutat Res 157:123-128.

Laflamme, RE; Hites, RA. (1978) The global distribution of polycyclic aromatic hydrocarbons in recent sediments. Geochim Cosmochim Acta 42:89-310.

Lee, FS-C; Schuetzle, D. (1983) Sampling, extraction, and analysis of polycyclic aromatic hydrocarbons from internal combustion engines. In: Bjørseth, A, ed. Handbook of polycyclic aromatic hydrocarbons. New York: Marcel Dekker, Inc.; pp. 27-94.

Lee, FSC; Pierson, WR; Ezike, J. (1980) The problem of PAH degradation during filter collection of airborne particulates—an evaluation of several commonly used filter media. In: Bjørseth, A; Dennis, AJ, eds. Polynuclear aromatic hydrocarbons: chemistry and biological effects; proceedings of the 4th international symposium; Columbus, OH. Columbus, OH: Battelle Press, pp. 543-563.

Levsen, K. (1988) The analysis of diesel particulate. Fresenius Z Anal Chem 331:467-478.

Liberti, A; Ciccioli, P; Cecinato, A; Brancaleoni, E; Di Palo, C. (1984) Determination of nitrated-polyaromatic hydrocarbons (nitro-PAHs) in environmental samples by high resolution chromatographic techniques. J High Resolut Chromatogr Commun 7:389-397.

Ligocki, MP; Pankow, JF. (1989) Measurements of the gas/particle distributions of atmospheric organic compounds. Environ Sci Technol 23:75-83.

Ligocki, MP; Leuenberger, C; Pankow, JF. (1985a) Trace organic compounds in rain—II. Gas scavenging of neutral organic compounds. Atmos Environ 19:1609-1617.

Ligocki, MP; Leuenberger, C; Pankow, J. (1985b) Trace organic compounds in rain—III. Particle scavenging of neutral organic compounds. Atmos Environ 19:1619-1629.

Lipkea, WH; DeJoode, AD. (1987) A model of a direct injection diesel combustion system for use in cycle simulation and optimization studies. Presented at: International congress and exposition; February; Detroit, MI. Warrendale, PA: Society of Automotive Engineers, Inc., SAE technical paper no. 870573.

Lipkea, WH; DeJoode, AD; Christenson, SR. (1987) The relationship between nitric oxide and work as influenced by engine operating conditions and combustion system parameters for a direct injection diesel engine. Presented at:

International congress and exposition; February; Detroit, MI. Warrendale, PA: Society of Automotive Engineers, Inc., SAE technical paper no. 870269.

Löfroth, G. (1981) Comparison of the mutagenic activity in carbon particulate matter and in diesel and gasoline engine exhaust. In: Waters, MD; Sandhu, SS; Huisingh, JL; Claxton, L; Nesnow, S, eds. Short-term bioassays in the analysis of complex environmental mixtures II: proceedings of the second symposium on the application of short-term bioassays in the fractionation and analysis of complex environmental mixtures; March 1980; Williamsburg, VA. (Hollaender, A; Welch, BL; Probstein, RF, eds. Environmental science research series: v. 22). New York: Plenum Press; pp. 319-336.

Lowenthal, DH; Rahn, KA. (1985) Regional sources of pollution aerosol at Barrow, Alaska during winter 1979-80 as deduced from elemental tracers. Atmos Environ 19:2011-2024.

Lyn, WT. (1960-61) Calculation of the effect of rate of heat release on the shape of cylinder pressure diagram and cycle efficiency. Proc Automob Div Inst Mech Eng (1).

Lyn, WT. (1963) Study of burning rate and nature of combustion in a diesel engine. In: Ninth international symposium on combustion. New York: Academic Press, Inc.

Lyn, WT; Valdmanis, E. (1966-67) The effect of physical factors on ignition delay. Proc Inst Mech Eng Part 2A (1).

McCann, J; Ames, BN. (1977) The *Salmonella*/microsome mutagenicity test: predictive value for animal carcinogenicity. In: Hiatt, HH; Watson, JD; Winsten, JA, eds. Origins of human cancer: book C, human risk assessment. (Cold Spring Harbor conferences on cell proliferation: v. 4). New York: Cold Spring Harbor Laboratory, pp. 1431-1450.

McClellan, RO. (1986) Health effects of diesel exhaust: a case study in risk assessment. Am Ind Hyg Assoc J 47:1-13.

McCoy, EC; Rosenkranz, HS; Mermelstein, R. (1981) Evidence for the existence of a family of bacterial nitroreductases capable of activating nitrated polycyclics to mutagens. Environ Mutagen 3:421-427.

McVeety, BD; Hites, RA. (1988) Atmospheric deposition of polycyclic aromatic hydrocarbons to water surfaces: a mass balance approach. Atmos Environ 22:511-536.

Miguel, AH; Pereira, PAP. (1989) Benzo(k)fluoranthene, benzo(ghi)perylene, and indeno(1,2,3-cd)pyrene: new tracers of automotive emissions in receptor modeling. Aerosol Sci Technol 10:292-295.

Myers, PS; Uyehara, OA. (1947) Flame temperature measurements—electronic solution of temperature equations. SAE Q Trans 1:592-611.

National Research Council. (1982) Diesel cars: benefits, risks and public policy, final report of the Diesel Impacts Study Committee. Washington, DC: National Academy Press.

Newton, DL; Erickson, MD; Tomer, KB; Pellazzari, ED; Gentry, P; Zweidinger, RB. (1982) Identification of nitroaromatics in diesel exhaust particulate using gas chromatography/negative ion chemical ionization mass spectrometry and other techniques. Environ Sci Technol 16:206-213.

Nielsen, T. (1988) The decay of benzo[*a*]pyrene and cyclopenteno(*cd*)pyrene in the atmosphere. Atmos Environ 22:2249-2254.

Nishioka, MG; Petersen, B; Lewtas, J. (1983) Comparison of nitro-aromatic content and direct-acting mutagenicity of passenger car engine emissions. In: Rondia, D; Cooke, M; Haroz, RK, eds. Mobile source emissions including polycyclic organic species. (NATO advanced science institutes series C, mathematical and physical sciences: v. 112). Dordrecht, The Netherlands: D. Reidel, pp. 197-210.

Obert, EF. (1973) Internality of diesel particulate matter a sampling artifact? Environ Sci Technol 17:621-624.

Okamoto, WK; Gorse, RA, Jr; Pierson, WR. (1983) Nitric acid in diesel exhaust. J Air Pollut Control Assoc 33: 1098-1100.

Pankow, JF; Isabelle, LM; Asher, WE. (1984) Trace organic compounds in rain. 1. Sampler design and analysis by adsorption/thermal desorption (ATD). Environ Sci Technol 18:310-318.

Paputa-Peck, MC; Marano, RS; Schuetzle, D; Riley, TL; Hampton, CV; Prater, TJ; Skewes, LM; Jensen, TE; Ruehle, PH; Bosch, LC; Duncan, WP. (1983) Determination of nitrated polynuclear aromatic hydrocarbons in particulate extracts by capillary column gas chromatography with nitrogen selective detection. Anal Chem 55: 1946-1954.

Pierson, WR; Brachaczek, WW. (1976) Particulate matter associated with vehicles on the road. Warrendale, PA: Society of Automotive Engineers; SAE technical paper no. 760039. SAE Trans 85:209-227.

Pierson, WR; Brachaczek, WW. (1983a) Emissions of ammonia and amines from vehicles on the road. Environ Sci Technol 17:757-760.

Pierson, WR; Brachaczek, WW. (1983b) Particulate matter associated with vehicles on the road. II. Aerosol Sci Technol 2:1-40.

Pierson, WR; Brachaczek, WW; Hammerle, RH; McKee, DE; Butler, JW. (1978) Sulfate emissions from vehicles on the road. J Air Pollut Control Assoc 28:123-132.

Pierson, WR; Brachaczek, WW; McKee, DE. (1979) Sulfate emissions from catalyst-equipped automobiles on the highway. J Air Pollut Control Assoc 29:255-257.

Pierson, WR; Gorse, RA, Jr; Szkarlat, AC; Brachaczek, WW; Japar, SM; Lee, FS-C; Zweidinger, RB; Claxton, LD. (1983) Mutagenicity and chemical characteristics of carbonaceous particulate matter from vehicles on the road. Environ Sci Technol 17:31-44.

Pitts, JN, Jr; Grosjean, D; Mischke, TM; Simmon, VF; Poole, D. (1977) Mutagenic activity of airborne particulate organic pollutants. Toxicol Lett 1:65-70.

Pitts, JN, Jr; Van Cauwenberghe, KA; Grosjean, D; Schmid, JP; Fitz, DR; Belser, WL, Jr; Knudson, GB; Hynds, PM. (1978) Atmospheric reactions of polycyclic aromatic hydrocarbons: facile formation of mutagenic nitro derivatives. Science (Washington, DC) 202:515-519.

Pitts, JN, Jr; Lokensgard, DM; Ripley, PS; Van Cauwenberghe, KA; Van Vaeck, L; Shaffer, SD; Thill, AJ; Belser, WL, Jr. (1980) "Atmospheric" epoxidation of benzo[a]pyrene by ozone: formation of the metabolite benzo[a]pyrene-4,5-oxide. Science (Washington, DC) 210:1347-1349.

Pitts, JN, Jr; Sweetman, JA; Zielinska, B; Winer, AM; Atkinson, R. (1985a) Determination of 2-nitrofluoranthene and 2-nitropyrene in ambient particulate organic matter: evidence for atmospheric reactions. Atmos Environ 19:1601-1608.

Pitts, JN, Jr; Zielinska, B; Sweetman, JA; Atkinson, R; Winer, AM. (1985b) Reaction of adsorbed pyrene and perylene with gaseous N_2O_5 under simulated atmospheric conditions. Atmos Environ 19:911-915.

Pitts, JN, Jr; Sweetman, JA; Zielinska, B; Atkinson, R; Winer, AM; Harger, WP. (1985c) Formation of nitroarenes from the reaction of polycyclic aromatic hydrocarbons with dinitrogen pentoxide. Environ Sci Technol 19:1115-1121.

Pitts, JN, Jr; Paur, H-R; Zielinska, B; Arey, J; Winer, AM; Ramdahl, T; Mejia, V. (1986) Factors influencing the reactivity of polycyclic aromatic hydrocarbons adsorbed on filters and ambient POM with ozone. Chemosphere 15:675-685.

Ramdahl, T; Zielinska, B; Arey, J; Atkinson, R; Winer, A; Pitts, JN, Jr. (1986) Ubiquitous occurrence of 2-nitrofluoranthene and 2-nitropyrene in air. Nature (London) 231:425-427.

Rogge, W; Mazurek, MA; Hildemann, LM; Cass, GR. (1993) Quantification of urban organic aerosols at a molecular level: identification, abundance and seasonal variation. Atmos Env 27A:1309-1330.

Rosenkranz, HS; Mermelstein, R. (1983) Mutagenicity and genotoxicity of nitroarenes: all nitro-containing chemicals were not created equal. Mutat Res 114:217-267.

Ross, MM; Risby, TH; Steele, WA; Lestz, SS; Yasbin, RE. (1982) Physicochemical properties of diesel particulate matter. Colloids Surf 5:17-31.

Salmeen, IT; Pero, AM; Zator, R; Schuetzle, D; Riley, TL. (1984) Ames assay chromatograms and the identification of mutagens in diesel particle extracts. Environ Sci Technol 18:375-382.

Salmeen, IT; Gorse, RA, Jr; Pierson, WR. (1985) Ames assay chromatograms of extracts of diesel exhaust particles from heavy-duty trucks on the road and from passenger cars on a dynamometer. Environ Sci Technol 19: 270-273.

Schroeder, WH; Lane, DA. (1988) The fate of toxic airborne pollutants: the atmosphere plays a major role in their transformation and transport. Environ Sci Technol 22:240-246.

Schuetzle, D. (1983) Sampling of vehicle emissions for chemical analysis and biological testing. Environ Health Perspect 47:65-80.

Schuetzle, D. (1988) Organic tracers for source apportionment of combustion emissions to ambient air particulates. In: proceedings of the sixth symposium on environmental analytical chemistry and source apportionment in ambient and indoor atmospheres; June; Provo, UT.

Schuetzle, D; Perez, JM. (1981) A CRC cooperative comparison of extraction and HPLC techniques for diesel particulate emissions. Presented at: 74th annual meeting of the Air Pollution Control Association; June; Philadelphia, PA. Pittsburgh, PA: Air Pollution Control Association; paper no. 81-56.4.

Schuetzle, D; Perez, JM. (1983) Factors influencing the emissions of nitrated-polynuclear aromatic hydrocarbons (nitro-PAH) from diesel engines. J Air Pollut Control Assoc 33:751-755.

Schuetzle, D; Jensen, TE. (1985) Analysis of nitrated polycyclic aromatic hydrocarbons by mass spectrometry. In: White, C. M., ed. Nitrated polycyclic aromatic hydrocarbons. Heidelberg, Germany: A. Huthing Verlag, pp. 121-167.

Schuetzle, D; Frazier, JA. (1986) Factors influencing the emission of vapor and particulate phase components from diesel engines. In: Ishinishi, N; Koizumi, A; McClellan, RO; Stöber, W, eds. Carcinogenic and mutagenic effects of diesel engine exhaust: proceedings of the international satellite symposium on toxicological effects of emissions from diesel engines; July; Tsukuba Science City, Japan. (Developments in toxicology and environmental science: v. 13). Amsterdam: Elsevier Science Publishers B. V., pp. 41-63.

Schuetzle, D; Lewtas, J. (1986) Bioassay-directed chemical analysis in environmental research. Anal Chem 58: 1060A-1076A.

Schuetzle, D; Lee, FS-C; Prater, TJ; Tejada, SB. (1981) The identification of polynuclear aromatic hydrocarbon (PAH) derivatives in mutagenic fractions of diesel particulate extracts. Int J Environ Anal Chem 9:93-144.

Schuetzle, D; Riley, TL; Prater, TJ; Harvey, TM; Hunt, DF. (1982) Analysis of nitrated polycyclic aromatic hydrocarbons in diesel particulates. Anal Chem 54:265-271.

Schuetzle, D; Jensen, TE; Ball, JC. (1985) Polar PAH derivatives in extracts of particulates: biological characterization and techniques for chemical analysis. Environ Int 11:169-181.

Schulz, B. (1988) The United States engine markets in perspective. Diesel Prog N Am 53(6):8,10,12.

Shahed, SM. (1985) The role of fuel-air mixing in diesel combustion and emissions. ASME international conference on flows in internal combustion engines III, v. 28, pp. 159-164.

Siak, J; Chan, TL; Gibson, TL; Wolff, GT. (1985) Contribution to bacterial mutagenicity from nitro-PAH compounds in ambient aerosols. Atmos Environ 19:369-376.

Sienicki, EJ; Mago, RS. (1992) Re-evaluation of diesel particulate matter inventories. In: Toxic air pollutants from mobile sources: proceedings of an international specialty conference. Pittsburgh, PA: Air and Waste Management Association, pp. 151-164.

Siegla, DC; Smith, GW, eds. (1980) Particulate carbon: formation during combustion; proceedings of an international symposium; October 1980; Warren, MI. New York: Plenum Press.

Sigsby, JE, Jr; Tejada, S; Ray, W; Lang, JM; Duncan, JW. (1987) Volatile organic compound emissions from 46 in-use passenger cars. Environ Sci Technol 21:466-475.

Simoneit, BRT. (1984) Organic matter of the troposphere—III. Characterization and sources of petroleum and pyrogenic residues in aerosols over the western United States. Atmos Environ 18:51-67.

Slinn, WGN; Hasse, L; Hicks, BB; Hogan, AW; Lal, D; Liss, PS; Munnich, KO; Sehmel, GA; Vittori, O. (1978) Some aspects of the transfer of atmospheric trace constituents past the air-sea interface. Atmos Environ 12: 2055-2087.

Smith, LR. (1989) Characterization of exhaust emissions from trap-equipped light-duty diesels [final report]. Sacramento, CA: California Air Resources Board; contract no. A5-159-32.

Smith, LR; Paskind, J. (1989) Characterization of exhaust emissions from trap-equipped light-duty diesels. Presented at: Passenger car meeting and exposition; September; Dearborn, MI. Warrendale, PA: Society of Automotive Engineers, Inc.; SAE technical paper no. 891972.

Sonnefeld, WJ; Zoller, WH; May, WE. (1983) Dynamic coupled-column liquid chromatographic determination of ambient temperature vapor pressures of polynuclear aromatic hydrocarbons. Anal Chem 55:75-280.

Springer, KJ. (1988) Diesel lube oils—4th dimension of diesel particulate control. In: Springer, KJ, ed. Engine emission technology for the 1990's; proceedings of the internal combustion engine division technical conference; October; San Antonio, TX. New York: American Society of Mechanical Engineers, pp. 45-51.

Springer, KJ. (1989) Low emission diesel fuel for 1991—1994. In: Chrisman, B; Serve, JV, eds. Advances in engine emissions control technology ICE, v. 5. New York; American Society of Mechanical Engineers.

Stockwell, WR; Calvert, JG. (1983) The mechanism of the HO-SO$_2$ reaction. Atmos Environ 17:2231-2235.

Sweetman, JA; Zielinska, B; Atkinson, R; Ramdahl, T; Winer, AM; Pitts, JN, Jr. (1986) A possible formation pathway for the 2-nitrofluoranthene observed in ambient particulate organic matter. Atmos Environ 20:235-238.

Szkarlat, AC; Japar, SM. (1983) Optical and chemical properties of particle emissions from on-road vehicles. J Air Pollut Control Assoc 33:592-597.

Talcott, R; Wei, E. (1977) Airborne mutagens bioassayed in *Salmonella typhimurium*. J Natl Cancer Inst 58:449-451.

Thrane, KE; Mikalsen, A. (1981) High-volume sampling of airborne polycyclic aromatic hydrocarbons using glass fibre filters and polyurethane foam. Atmos Environ 15:909-918.

Tokiwa, H; Takeyoshi, H; Morita, K; Takahashi, K; Saruta, N; Ohnishi, Y. (1976) Detection of mutagenic activity in urban air pollutants. Mutat Res 38:351.

Tokiwa, H; Morita, K; Takeyoshi, H; Takahashi, K; Ohnishi, Y. (1977) Detection of mutagenic activity in particulate air pollutants. Mutat Res 48:237-248.

Tokiwa, H; Kitamori, S; Takahashi, K; Ohnishi, Y. (1980) Mutagenic and chemical assay of extracts of airborne particulates. Mutat Res 77:99-108.

Tokiwa, H; Kitamori, S; Nakagawa, R; Horikawa, K; Matamala, L. (1983) Demonstration of a powerful mutagenic dinitropyrene in airborne particulate matter. Mutat Res 121:107-116.

Tong, HY; Karasek, FW. (1984) Quantitation of polycyclic aromatic hydrocarbons in diesel exhaust particulate matter by high-performance liquid chromatography fractionation and high-resolution gas chromatography. Anal Chem 56:2129-2134.

Tong, HY; Sweetman, JA; Karasek, FW; Jellum, E; Thorsrud, AK. (1984) Quantitative analysis of polycyclic aromatic compounds in diesel exhaust particulate extracts by combined chromatographic techniques. J Chromatogr 312:183-202.

Tosaka, S; Fujiwara, Y; Murayama, T. (1989) The effect of fuel properties on diesel engine exhaust particulate formation. Presented at: International congress and exposition; February-March; Detroit, MI. Warrendale, PA: Society of Automotive Engineers, Inc., SAE technical paper no. 890421.

Truex, TJ; Pierson, WR; McKee, DE; Shelef, M; Baker, RE. (1980) Effects of barium fuel additive and fuel sulfur level on diesel particulate emissions. Environ Sci Technol 14:1121-1124.

Ullman, TL. (1989) Investigation of the effects of fuel composition on heavy-duty diesel engine emissions. Presented at: International fuels and lubricants meeting and exposition; September; Baltimore, MD. Warrendale, PA: Society of Automotive Engineers, Inc., SAE technical paper no. 892072.

U.S. Environmental Protection Agency. (1985) Compilation of air pollutant emission factors, volume I: stationary point and area sources; volume II: mobile sources. 4th ed. Research Triangle Park, NC: Office of Air Quality Planning and Standards; EPA report no. AP-42-ED-4-VOL-1 and AP-42-ED-4-VOL-2. Available from: NTIS, Springfield, VA; PB86-124906 and PB87-205266.

U.S. Environmental Protection Agency. (1986) Program to calculate size specific particulate emissions for mobile sources. Ann Arbor, MI: Emission Control Technology Division; EPA report no. EPA/SW/MT-86/011. Available from: NTIS, Springfield, VA; PB86-179702/XAB.

U.S. Environmental Protection Agency. (1989) User's guide to MOBILE4 (Mobile Source Emissions Factor Model). Ann Arbor, MI: Office of Mobile Sources; EPA report no. EPA-AA-TEB-89-01. Available from: NTIS, Springfield, VA; PB89-164271.

U.S. Environmental Protection Agency. (1993) Motor vehicle-related air toxic study. Ann Arbor, MI: Office of Mobile Sources. EPA/420/R-93/005. Available from National Technical Information Service, Springfield, VA, PB93-182590/XAB.

Uyehara, OA. (1987) Factors that affect BSFC and emissions for diesel engines: part 1—presentation of concepts. Presented at: International congress and exposition; February; Detroit, MI. Warrendale, PA: Society of Automotive Engineers, Inc., SAE technical paper no. 870343.

Van Vaeck, L; Van Cauwenberghe, K. (1984) Conversion of polycyclic aromatic hydrocarbons on diesel particulate matter upon exposure to ppm levels of ozone. Atmos Environ 18:323-328.

Van Vaeck, L; Van Cauwenberghe, K; Janssens, J. (1984) The gas-particle distribution of organic aerosol constituents: measurements of the volatilisation artefact in hi-vol cascade impactor sampling. Atmos Environ 18:417-430.

Wade, WR; Jones, CM. (1984) Current and future light duty diesel engines and their fuels. Presented at: International congress and exposition; February-March; Detroit, MI. Warrendale, PA: Society of Automotive Engineers, Inc., SAE technical paper no. 840105.

Warner-Selph, MA; Dietzmann, HE. (1984) Characterization of heavy-duty motor vehicle emissions under transient driving conditions. Research Triangle Park, NC: U.S. Environmental Protection Agency, contract no. 68-02-3722.

Watson, JG; Robinson, NF; Chow, JC; Henry, RC; Kim, BM; Pace, TG; Meyer, EL; Nguyen, Q. (1990) The USEPA/DRI chemical mass balance receptor model, CMB 7.0. Environ Software 5:38-49.

Westerholm, RN; Almén, J; Li, H; Rannug, JU; Egebäck, K-E; Grägg, K. (1991) Chemical and biological characterization of particulate-, semivolatile-, and gas-phase-associated compounds in diluted heavy-duty diesel exhausts: a comparison of three different semivolatile-phase samplers. Environ Sci Technol 25:332-338.

White, CM. (1983) Determination of polycyclic aromatic hydrocarbons in coal-derived materials. In: Bjørseth, A, ed. Handbook of polycyclic aromatic hydrocarbons. New York, NY: Marcel Dekker, Inc.; pp. 525-616.

White, CM. (1985) Analysis of nitrated polycyclic aromatic hydrocarbons by gas chromatography. In: White, C. M., ed. Nitrated polycyclic aromatic hydrocarbons. Heidelberg, Germany: A. Huthing Verlag, pp. 1-86.

Williams, DJ; Milne, JW; Roberts, DB; Kimberlee, MC. (1989a) Particulate emissions from 'in-use' motor vehicles—I. Spark ignition vehicles. Atmos Environ 23:2639-2645.

Williams, DJ; Milne, JW; Quigley, SM; Roberts, DB; Kimberlee, MC. (1989b) Particulate emissions from 'in-use' motor vehicles—II. Diesel vehicles. Atmos Environ 23:2647-2661.

Wu, KJ; Peterson, RC. (1986) Correlation of nitric oxide emission from a diesel engine with measured temperature and burning rate. Presented at: International fuels and lubricants meeting and exposition; October; Philadelphia, PA. Warrendale, PA: Society of Automotive Engineers, Inc., SAE technical paper no. 861566.

Yamasaki, H; Kuwata, K; Miyamoto, H. (1982) Effects of ambient temperature on aspects of airborne polycyclic aromatic hydrocarbons. Environ Sci Technol 16:189-194.

Yamasaki, H; Kuwata, K; Kuge, Y. (1984) Determination of vapor pressure of polycyclic aromatic hydrocarbons in the supercooled liquid phase and their adsorption on airborne particulate matter. Nippon Kagaku Kaishi 8:1324-1329.

Yokley, RA; Garrison, AA; Wehry, EL; Mamantov, G. (1986) Photochemical transformation of pyrene and benzo[a]pyrene vapor-deposited on eight coal stack ashes. Environ Sci Technol 20:86-90.

Yost, DM; Ryan, TW, III; Owens, EC. (1985) Fuel effects on combustion in a two-stroke diesel engine. Presented at: International fuels and lubricants meeting and exposition; October; Tulsa, OK. Warrendale, PA: Society of Automotive Engineers, Inc., SAE technical paper no. 852104.

Yu, M-L; Hites, RA. (1981) Identification of organic compounds on diesel engine soot. Anal Chem 53:951-954.

Yu, RC; Shahed, SM. (1981) Effects of injection timing and exhaust gas recirculation on emissions from a D.I. diesel engine. Presented at: Fuels and lubricants meeting; October; Tulsa, OK. Warrendale, PA: Society of Automotive Engineers, Inc., SAE technical paper no. 811234.

Zielinska, B; Arey, J; Atkinson, R; Ramdahl, T; Winer, AM; Pitts, JN, Jr. (1986) Reaction of dinitrogen pentoxide with fluoranthene. J Am Chem Soc 108:4126-4132.

Zielinska, B; Arey, J; Atkinson, R; McElroy, PA. (1988) Nitration of acephenanthrylene under simulated atmospheric conditions and in solution and the presence of nitroacephenanthrylene(s) in ambient particles. Environ Sci Technol 22:1044-1048.

Zielinska, B; Arey, J; Atkinson, R; McElroy, PA. (1989a) Formation of methylnitronaphthalenes from the gas-phase reactions of 1- and 2-methylnaphthalene with OH radicals and N_2O_5 and their occurrence in ambient air. Environ Sci Technol 23:723-729.

Zielinska, B; Arey, J; Atkinson, R; Winer, AM. (1989b) The nitroarenes of molecular weight 247 in ambient particulate samples collected in southern California. Atmos Environ 23:223-229.

Zielinska, RB; Sigsby, JE, Jr; Tejada, SB; Stump, FD. (1990) The atmospheric formation of nitroarenes and their occurence in ambient air. In: Proceedings of the fourth international conference on N-substituted aryl compounds: occurrence, metabolism and biological impact of nitroarenes; July 1989; Cleveland, OH.

Zweidinger, RB; Sigsby, JE, Jr; Tejada, SB; Stump, FD; Dropkin, DL; Ray, WD; Duncan, JW. (1988) Detailed hydrocarbon and aldehyde mobile source emissions from roadway studies. Environ Sci Technol 22:956-962.